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Substitute Chemical Program. Initial Scientific Review of MSMA/DSMA

Midwest Research Inst.

Prepared For
Environmental Protection Agency

December 1975

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PB 251 566

SUBSTITUTE CHEMICAL PROGRAM

INITIAL SCIENTIFIC REVIEW OF MSMA/DSMA

DECEMBER 1975

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDE PROGRAMS
CRITERIA AND EVALUATION DIVISION
WASHINGTON, D.C. 20460

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PREFACE

The Alternative (Substitute) Chemicals Program was initiated under Public Law 93-135 of October 24, 1973, to "provide research and testing of substitute chemicals." The legislative intent is to prevent using substitutes which in essence are more deleterious to man and his environment than a "problem" pesticide suspected of causing "unreasonable adverse effects to man or his environment." The major objective of the program is to determine the suitability of potential substitute chemicals which now or in the future may act as replacements for those uses (major or minor) of pesticides that have been cancelled, suspended, or are in litigation or under internal review for potential unreasonable adverse effects on man and his environment.

The substitute chemical is reviewed for suitability considering all applicable scientific factors, such as chemistry, toxicology, pharmacology, environmental fate and movement, use patterns and efficacy. EPA recognizes the fact that even though a compound is registered, it still may not be a practical substitute for a particular use or uses of a problem pesticide. The utilitarian value of the "substitute" must be evaluated by reviewing its biological and economic data. The reviews of substitute chemicals are carried out in two phases. Phase I conducts these reviews based on data bases readily accessible at the present time. An Initial Scientific Review is conducted to make a judgment with respect to the "safety and efficacy" of the substitute chemical. The Phase II Integrated Use Analysis examines the situation resulting from possible regulatory action against a hazardous pesticide for each of its major and critical uses. This Phase II analysis considers the suitable substitutes reviewed during Phase I in conjunction with alternative management practices to evaluate current and projected environmental, health, and economic impacts of potential changes in pest management practices.

The report summarizes rather than interprets scientific data reviewed during the course of the studies. Data is not correlated from different sources. Opinions are not given on contradictory findings.

This report contains the Phase I Initial Scientific Review of MSMA/DSMA. MSMA/DSMA were identified as registered substitute chemicals for certain cancelled and suspended uses of 2,4,5-T. The report covers all uses of MSMA/DSMA and is intended to be adaptable to future needs. Should MSMA/DSMA be identified as substitutes for a problem pesticide other than 2,4,5-T, the report can be updated and made readily available for use. The data contained in this report was not intended to be complete in all areas. Data searches ended in January, 1975.

The review was coordinated by a team of EPA scientists in the Criteria and Evaluation Division of the Office of Pesticide Programs. The responsibility of the team leader was to provide guidance and direction and technically review information retrieved during the course of the study. The following EPA scientists were members of the review team: Fumihiko Hayashi, Ph.D. (Team Leader); George Beusch (Chemistry); William Burnam (Pharmacology and Toxicology);

John Bowser (Fate and Significance in the Environment); Richard Petrie (Fate and Significance in the Environment); Charles Lewis (Registered Uses); and Jeff Conopask, Ph.D. (Economics).

Data research, abstracting, and collection were primarily performed by Midwest Research Institute (MRI), Kansas City, Missouri (EPA Contract #68-01-2448) under the direction of Mr. Thomas L. Ferguson. RvR Consultants, Shawnee Mission, Kansas, under a subcontract to MRI, assisted in data collection. The following MRI scientists were principal contributors to the report: James V. Dilley, Ph.D., John Doull, Ph.D., David Hahlen, William B. House, Ph.D., Thomas L. Ferguson and Alfred F. Meiners. Rosemarie von Rumker, Ph.D., (RvR Consultants) also contributed to the report.

Draft copies of the report have been reviewed by the scientific staffs of EPA's National Environmental Research Centers and their associated laboratories. Comments and supplemental material provided by the following laboratories were greatly appreciated and have been incorporated into this report: Gulf Breeze Environmental Research Laboratory, Gulf Breeze, Florida, and National Ecological Research Laboratory, Corvallis, Oregon. The Ansul Company and Diamond Shamrock Chemical Company, manufacturers of MSMA/DSMA, reviewed the draft of this report and made certain comments and additions.

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This section contains a summary of the "Initial Scientific Review" conducted on MSMA (monosodium methanearsonate) and DSMA (disodium methanearsonate). The section summarizes rather than interprets data reviewed.

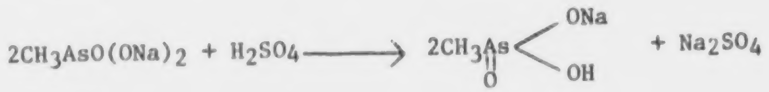
Production and Use

DSMA (disodium methanearsonate) is manufactured by a synthesis process involving two reactions:

$$As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O$$

$$Na_3AsO_3 + CH_3Cl \longrightarrow \underset{\text{DSMA}}{CH_3AsO(ONa)_2} + NaCl$$

MSMA (monosodium methanearsonate) is then made from DSMA by treatment with sulfuric acid:



$$\underset{\text{DMSA}}{2CH_3AsO(ONa)_2} + H_2SO_4 \longrightarrow \underset{\text{MSMA}}{2CH_3\underset{\overset{\|}{O}}{As}\begin{matrix}\diagup ONa\\ \diagdown OH\end{matrix}} + Na_2SO_4$$

DMSA MSMA

DSMA is also an intermediate used in the production of various other salts of methylarsonic acid (MAA).

MSMA and DSMA undergo few chemical reactions. These compounds are in a stable oxidation state; strong oxidizing or reducing agents are required for chemical decomposition. However, there is disagreement over whether mixing MSMA or DSMA with "hard" water (i.e., water containing relatively high concentrations of calcium) could cause precipitation of insoluble calcium methanearsonate.

DSMA readily absorbs water from the air to form a crystalline hexahydrate, one form in which it is marketed. Both DSMA and MSMA are also sold as solutions of various strengths and combinations with other herbicides.

MSMA and DSMA are used mainly as contact herbicides to control a number of hard-to-control weeds including Johnson grass, nutsedge, dallisgrass, and crabgrass, as well as several other weeds. The herbicides are also used for directed application (having no contact with crop plants) on citrus fruits (bearing and non-bearing) and on cotton. DSMA is also registered for use as a topical application (allowing for contact with crop plants) on cotton. MSMA is registered for use as a directed application in non-bearing deciduous fruit and nut orchards. MSMA and DSMA are both used on lawns, ornamental grass and certain noncrop areas, as well. Tolerances for MSMA and DSMA have been established for citrus fruits and cottonseed and are pending for grapes and sugarcane.

According to the U.S. Tariff Commission, the production of all MAA salts was almost 30.7 million lb in 1972. Of this amount, 24.0 million lb (78%) were estimated to have been MSMA and 6.0 million lb (19%), DSMA. An estimated 7 million lb of the total were exported; negligible amounts, if any, were imported.

In 1972, an estimated 23 million lb of MSMA and DSMA were used in the United States. Midwest Research Institute (MRI) estimates that this total consisted of about 19 million lb of MSMA and 4 million lb of DSMA. About 15.5 million lb of MSMA and DSMA (about two-thirds of the total domestic consumption) were used by farmers, primarily for preplant and postemergence weed control on cotton. The remaining 7.5 million lb of MSMA and DSMA were used in industrial and commercial weed control by governmental agencies and for residential and home garden weed control.

By geographic regions, MRI estimates that about 70% of the total 1972 usage of MSMA and DSMA was in the South Central states, followed (in decreasing order of use) by the Southeastern, North Central, Southwestern, Northwestern, and Northeastern states.

Toxicity and Physiological Effects

Limited data was found on the toxicity and physiological effects of MSMA and DSMA. Background material is provided on closely related compounds, such as MAA (an equilibrium form of MSMA at low pH) and other possible metabolic products.

Reports on the toxicity of MSMA and DSMA to animals indicate that the compounds are low to moderately toxic. LD_{50} values obtained with rats for MSMA, DSMA, and related arsenicals are as follows:

Compound	Concentration (%)*	LD_{50} (g/kg)
MSMA	25.1	2.6
MSMA	51.55	1.8
MSMA	35.21	1.8
DSMA	65.66	2.8
MAA	98.8	1.4

---

* Concentrations tested have been included because available data did not always specify whether the LD_{50} was expressed in terms of the amount of arsenic, DSMA or MSMA, or formulation tested.

In most of the acute toxicity studies, gross pathological changes in tissues and organs were not observed in the survivors. However, moderate to severe gastroenteritis was noted in the animals that died.

Definitive acute toxicity data for laboratory animals other than the rat has not been reported.

In tests on rabbits MSMA and DSMA were reported to be mildly irritating to the skin.

The acute LD_{50} for MSMA (22.6 to 29.0%) in cattle was reported to be 1.7 g/kg body weight in 400-lb animals and 1.2 g/kg in calves.

Heifers (400 lb) were killed by a total dose of 78.7 oz of MSMA (21% arsenic) administered over 9 days or by 47.6 oz administered over 5 days. One heifer that was treated with MSMA (2 oz per day) died after 23 daily exposures.

No subacute toxicological effects were observed in rats fed MAA (52.3% arsenic) at dietary levels of 100 ppm for 90 days. In addition, the compound had no effect on dogs when fed at 90 ppm in the diet for 90 days.

The results of most studies indicate that, in the rat, a cumulative effect is evident from repeated dosing.

Although there is limited available data on animal metabolism of MSMA and DSMA, significant data has been reported on the metabolism of several related arsenical compounds. This data is presented as background information on arsenicals and does not necessarily apply to MSMA/DSMA:

1. Arsenic acid (H_3AsO_4) is excreted rapidly in the urine in man and cattle; there is little storage in tissues. The residue levels present in tissues rapidly decrease after the arsenicals are no longer fed or other exposure is stopped.

2. Some arsenic metabolites are not excreted in milk of cattle.

3. The extent of MSMA and DSMA concentration in tissues differs among rats, guinea pigs, rabbits, and hamsters. The rat is the only laboratory animal tested in which high concentrations of arsenic accumulated.

4. Some arsenic compounds do not accumulate in hens' eggs.

5. Pentavalent arsenic compounds appear to be more completely excreted than trivalent compounds.

6. Certain organic arsenicals, bound in animal tissues, are not released from these tissues to any great extent or stored in animals.

Effects of MSMA and DSMA on reproduction and teratogenic effects have not been studied. Sodium arsenate (a microbial metabolite of MSMA and DSMA) has been found to affect both resorption and malformation in the hamster.

Studies have not been reported on the oncogenic effects of MSMA and DSMA in rats or mice.

In field operations involving MSMA and DSMA, the arsenic levels in the urine of applicators have been shown to increase. However, the level decreases upon removal from source of application.

Food Tolerances and Acceptable Intake

Analytical methods which distinguish residues of specific arsenical compounds in plant materials are not presently being used. Foods and feed are analyzed for total arsenic (as As_2O_3); results, therefore, include naturally occurring arsenic levels in addition to pesticide residues.

There are currently tolerances for MSMA and DSMA on citrus fruits and cottonseed. Tolerances on grapes and sugarcane products are pending.

Investigators who have monitored the levels of arsenic in food and feed for a 6-yr period have concluded that the dietary intake of arsenic from pesticide residues is not significant.

Acceptable daily intakes (ADI) have not been established for MSMA or DSMA.

Environmental Effects

The data available concerning MSMA and DSMA's effects on fish is limited to toxicity studies. Only 6 species have been subjected to controlled study, and the number of replicate tests on these species is small. No reports were found on the effects of MSMA or DSMA to fish under field conditions. Published data on toxicity to fish is summarized as follows:

Species	Herbicide	LC_{50} 96-hr ppm
Bluegill (*Lepomis macrochirus*)	MSMA	49.2* > 1,000
Channel catfish (*Ictalurus punctatus*)	MSMA	26.8
Fathead minnow (*Pimephales promelas*)	MSMA	13.3
Goldfish (*Carassius auratus*)	MSMA	31.1
Rainbow trout (*Salmo gairdneri*)	MSMA	96.0

---

* Results from two separate investigations.

As with all pesticides having acute toxicity values for fish of greater than 1.0 ppm, commercial labels of MSMA and DSMA formulations do not carry any specific warnings regarding fish toxicity.

MSMA or DSMA (1.0 ppm in seawater) had no effect on pink shrimp (Penaeus duorarum) or Eastern oyster (Crassostrea virginica) after 48- and 24-hr exposures, respectively. A 96-hr exposure to 100 ppm of MSMA was not toxic to scud (Gammarus fasciatus).

Data on the effect of MSMA and DSMA on wildlife is also limited. Controlled studies have apparently been limited to 2 avian species.

The acute oral toxicities of DSMA to mallard ducks (Anas platyrhynchos) and bobwhite quail (Colinus virginianus) are >10,000 mg/kg and 3,160 mg/kg, respectively.

Subacute toxicity studies indicate that 10- to 15-day-old ducklings are not affected by dietary levels of 5,000 ppm MSMA. The dietary median lethal concentration (LC_{50}) for bobwhite quail was calculated to be 3,300 ppm of MSMA.

Studies have been made of the fate and environmental impact of organic arsenical herbicides (including MSMA) used in the forest environments of the Pacific Northwest. More than 400 determinations were made of arsenic residues in specific tissue and whole body samples from animals trapped at various intervals after use of the arsenicals. About 50% of the animals captured between 2 and 30 days following treatment contained arsenic residues between 0.5 and 9.8 ppm. One animal after 1 day of treatment contained arsenic residues ranging from 17 to 30 ppm in various body parts. Few animals collected more than 30 days after treatment contained detectable arsenic residues.

Both MSMA and DSMA have been classed as "relatively nontoxic" to honeybees (Apis mellifera), based on LD_{50} values determined from their contact effect when applied in the dust form. However, spraying with MSMA in aqueous solutions (equivalent to 4 lb active ingredient (AI) in 20 gal of water per acre) was reported to be "extremely toxic" to bees; mortality was about 70% 3 days after spraying. Oral ingestion of 100 and 1,000 ppm of MSMA and DSMA in sucrose syrup is also reported to be "extremely toxic" to the honeybee.

Soil microorganisms appear to be capable of degrading organic arsenical herbicides, including MSMA and DSMA. Penicillium brevicaule and Methanobacterium have been shown to produce methylarsines from methylarsonates. Studies using ^{14}C-labeled MSMA in 4 types of soil indicate a 2.4- to 14-fold increase in the degradation of MSMA (based on $^{14}CO_2$ evolution) when nonsterile soils are compared to steam-sterilized controls.

Tests have shown that soil concentrations of 50 ppm MSMA have no apparent toxicity to soil microbes.

Application of DSMA at an inordinate rate (9,992 lb/acre) apparently inhibits CO_2 evolution and bacterial growth, stimulates the growth of

Streptomyces, and inhibits somewhat the growth of soil fungi. The amount of organic matter available for microbial activity apparently has a direct effect on the rate of decomposition of these compounds in the soil.

Available data indicates that herbicidally-effective concentrations of MSMA and DSMA "disappear" rather rapidly from field soils after application. Microbial activity appears to some extent to contribute to their degradation; several different chemical reactions also appear to be involved. There is some disagreement among investigators concerning the relative importance of different chemical pathways, including reduction of the methylarsonates to form volatile methylarsines that escape in the atmosphere, and the formation of inorganic arsenates. Leaching of MSMA and DSMA through soil profiles appears to be inversely related to the soil clay content.

Numerous tests have reported the apparent tolerance of important crops to MSMA and DSMA residues in soils. DSMA at a rate of 120 lb AI/acre had no visible effect on barley, safflower, cotton, and sorghum for 3 successive years. MSMA at a rate of 256 lb AI/acre had no phytotoxic effect on lettuce, sugar beets, broccoli, or tomatoes planted 4 months after application; however, barley was affected.

Regarding MSMA and DSMA tests in water, one study reported the effect on stream water of MSMA use for forest thinning. No detectable residues were found in the water samples using an analytical technique sensitive to 0.01 ppm arsenic. Analysis of water following application of MSMA to irrigation-system ditch banks showed arsenic levels as high as 0.86 ppm immediately after application. Arsenic concentrations in the water, however, decreased as time progressed.

In bioaccumulation and biomagnification tests, one ongoing study has been reported concerning the effect of MSMA on a model micro-ecosystem containing daphnids (Daphnia magna), crayfish (Procambarus species), algae (Oedogonium cardiacum), and a channel catfish (Ictalurus punctatus). The crayfish in this system were reported to have bioconcentrated arsenic up to 10-fold from water containing 1 ppm MSMA. The single arsenical compound present in the crayfish (not MSMA) has not yet been identified.

Specific data on the environmental transport mechanisms for MSMA and DSMA was not found.

Efficacy and Performance Review

MSMA and DSMA are widely used for control of Johnson grass, nutsedge, dallisgrass, sandbur, and a wide variety of weedy grasses and broadleafed weeds. Although primarily used on cotton, the herbicides are also applied to weeds in citrus orchards, drainage ditches, rights of way, fence rows, storage yards, and other similar noncrop areas.

The efficacy and effectiveness of MSMA and DSMA vary with the weed being controlled. Generally, the rate and number of applications are the most important factors. With Johnson grass and nutsedge, single applications will give only temporary control and significant regrowth can be expected. Low temperatures appear to decrease the effectiveness of MSMA and DSMA, while sunlight and hot temperatures increase the rate of control.

At least 2 applications of DSMA are needed for good control of Johnson grass and a single application in the following season can provide up to 99% control. At least 2 lb/acre are needed per application. Control of Johnson grass often results in a regrowth of Bermuda grass which is not affected by DSMA or MSMA.

MSMA was found to give better control of nutsedge than DSMA. In comparable tests, regrowth was 89% in 3 weeks after application of DSMA and was 11% with MSMA. It was also found that purple nutsedge is more difficult to control than yellow nutsedge. Control is directly related to the number of applications and good control is achieved when applications are made at 2- to 4-week intervals during the season.

Close to 100% seasonal control of broadleaf weeds in cotton and better than 90% control of grasses was achieved with 3 to 4 direct applications of DSMA or MSMA.

A single directed application of MSMA or DSMA on cotton weeds can result in over 50% control of grasses, broadleaf weeds, and morning glory. This application reduces hoe labor by 60%.

PART II. INITIAL SCIENTIFIC REVIEW

SUBPART A. CHEMISTRY

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This section reviews available data on the chemistry of MSMA and DSMA and their presence in foods. Eight subject areas have been examined: Synthesis and Production Technology; Physical Properties; Analytical Methods; Composition and Formulation; Chemical Properties and Reactions; Occurence of Residues in Food and Feed Commodities; Acceptable Daily Intake, and Tolerances. The section summarizes rather than interprets data reviewed.

Synthesis and Production Technology

Methylarsonic Acid (MAA) and its salts have been known for over 90 years, having been first prepared by Meyer (1883).[1] However, the compounds were not used commercially until about 1956.

The original patent for use of sodium salts of various alkylarsonic acids as herbicides was issued to Arthur Schwerdle (1959).[2] Since then he has been issued patents for various other salts of MAA (Schwerdle 1962a,[3] 1962b,[4] 1962c,[5]), but the sodium salts are the most frequently used.

MSMA (Monosodium methanearsonate) is the most widely used of a group of organoarsenic herbicides introduced in the 1950's that also includes the octyl- and docecylammonium salts, the disodium salt (DSMA), and cacodylic acid (dimethylarsinic acid). The 2 major domestic manufacturers, The Ansul Company (Marinette, Wisconsin) and Diamond Shamrock Chemical Company (Green Bayou, Texas), as well as Vineland Chemical Company (Vineland, New Jersey) and W. A. Cleary Corporation (New Brunswick, New Jersey) all produce DSMA. DSMA can apparently serve as an intermediate in the manufacture of other organoarsenic herbicides.

Diamond Shamrock provided details on MSMA production (von Rümker et al. 1974).[6] The process is believed to be approximately as shown by the following reaction equations and by the production schematic shown in Figure 1:

---

[1] Meyer, G., Berichte der Deutsche Gesellschaft, Berlin, 16:1440 (1883).

[2] Schwerdle, A., U.S. Patent No. 2,889,347 (2 June 1959).

[3] Schwerdle, A. (to Vineland Chemical Company), U.S. Patent No. 3,030,199 (17 April 1962a).

[4] Schwerdle, A. (to Vineland Chemical Company), U.S. Patent No. 3,056,821 (2 October 1962b).

[5] Schwerdle, A. (to Vineland Chemical Company), U.S. Patent No. 3,068,088 (11 December 1962c).

[6] von Rümker, R., E. W. Lawless, and A. F. Meiners, Production, Distribution, Use, and Environmental Impact Potential of Selected Pesticides, for Council of Environmental Quality, Contract No. EQC-311 (15 March 1974).

$$As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O \qquad (1)$$

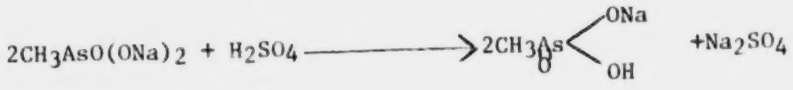
Arsenic
Trioxide

Sodium
Arsenite

$$Na_3AsO_3 + CH_3Cl \longrightarrow CH_3AsO(ONa)_2 + NaCl \qquad (2)$$

Methyl
Chloride

DSMA



$$2CH_3AsO(ONa)_2 + H_2SO_4 \longrightarrow 2CH_3\underset{\overset{\|}{O}}{As}\begin{matrix}ONa \\ OH\end{matrix} + Na_2SO_4 \qquad (3)$$

DSMA

MSMA

In the first step of the process, drums of arsenic trioxide are opened in an air-evacuated chamber and automatically dumped into the 50% caustic. A dust collection system is employed. The drums are washed carefully with water, the wash water is added to the reaction mixture, and the drums are crushed and are sold as scrap steel. The intermediate sodium arsenite is obtained as a 25% solution and is stored in large tanks prior to further reaction. In the next step, the 25% solution of sodium arsenite is treated with methyl chloride to give the disodium salt, DSMA.

In order to obtain MSMA, the solution is partially acidified with sulfuric acid and the resulting solution is concentrated by evaporation. The active ingredient is sold at a number of concentrations, but approximately 58% is the maximum concentration that can be prepared without encountering an undesirable increase in viscosity.

As the aqueous solution is being concentrated, a mixture of sodium sulfate and sodium chloride precipitates out, about 0.5 lb/100 lb AI. These salts, a troublesome disposal problem because they are contaminated with arsenic, are removed by centrifugation, washed in a 5-stage counter-current washing cycle, and then disposed of in a dump situated on nearly impermeable Beaumont clay which has no aqueous runoff.

Diamond Shamrock's plant is a "low effluent" plant, although aqueous waste is not discharged. Methanol, a side product of methyl chloride hydrolysis, is recovered and used elsewhere in the plant, and recovered water is recycled. Two equalization ponds are used and the discharge of arsenic averages about 0.7 to 0.8 ppm. The total amount of arsenic discharged amounts to only about 1/2 lb/day.

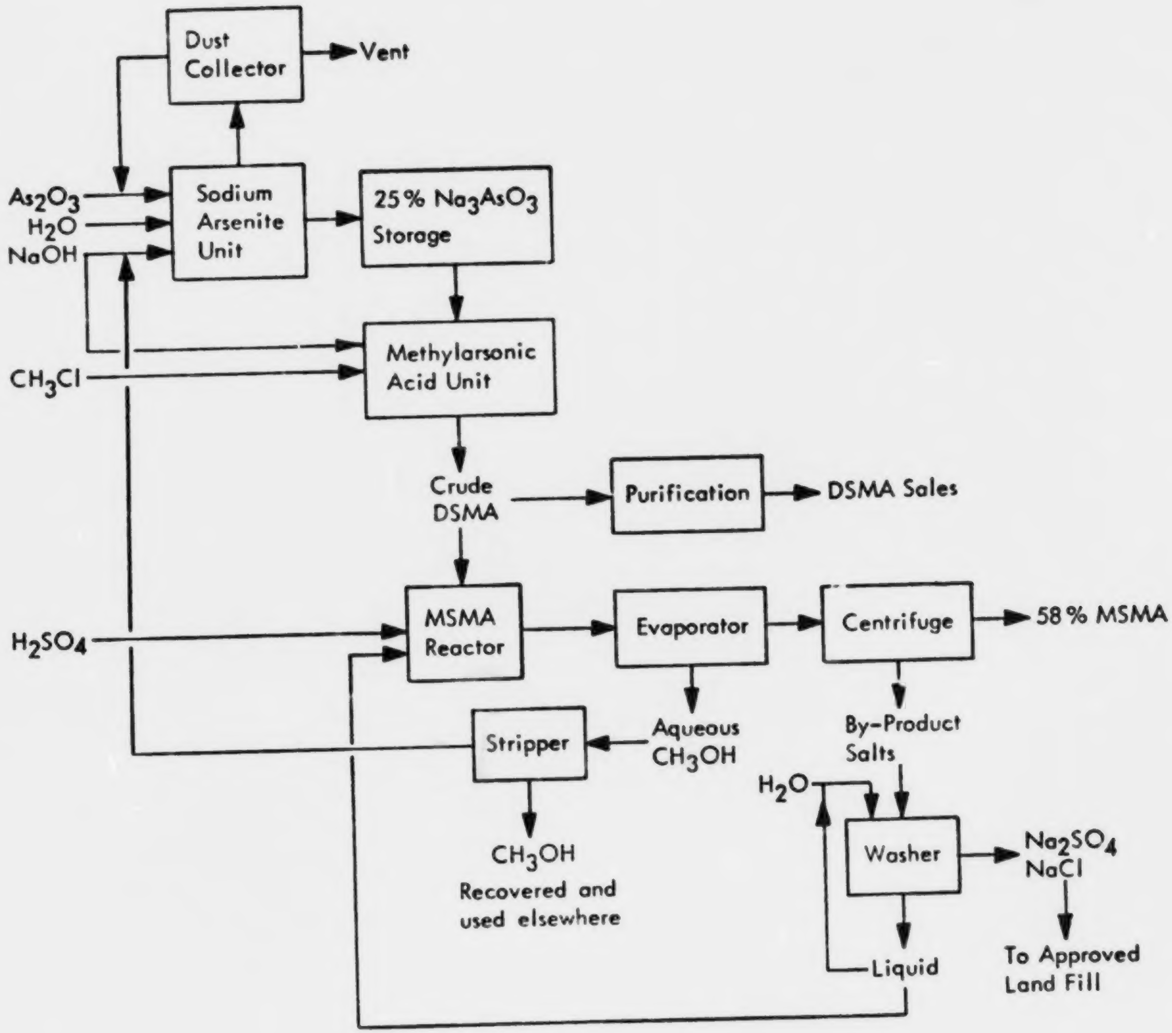

Dust Collector
Vent
As_2O_3
H_2O
NaOH
Sodium Arsenite Unit
25% Na_3AsO_3 Storage
CH_3Cl
Methylarsonic Acid Unit
Crude DSMA
Purification
DSMA Sales
H_2SO_4
MSMA Reactor
Evaporator
Centrifuge
58% MSMA
Aqueous CH_3OH
Stripper
CH_3OH Recovered and used elsewhere
By-Product Salts
H_2O
Washer
Na_2SO_4 NaCl
To Approved Land Fill
Liquid

Figure 1. Production schematic for MSMA and DSMA

Source: von Rümker et al., op. cit. (1974).

Other conditions and methods of manufacture are described in a U.S. patent by Urbanowski and Steinkoenig (1969).[1]

According to Urbanowski and Steinkoenig (1969), the reaction of sodium hydroxide with arsenic trioxide (Equation 1, p. 17) is not initially sent to completion with a stoichiometric ratio of sodium to arsenic (3.1:1); a lower sodium to arsenic ratio is used initially, and the balance of the sodium hydroxide is gradually added to the reaction in proportion to a gradual addition of methyl chloride (Equation 2, p. 17). This is done to minimize the hydrolysis of methyl chloride to methanol and thus maximize yield.

The methyl chloride is generally pumped to the reactor as a liquid and flashes to the gaseous state upon entering the reactor. The pressure (60 to 120 psig) is regulated by methyl chloride addition. Temperature is maintained at 60 to 90°C, because a temperature below 50°C can impair formation of DSMA, and a temperature above 100°C will cause product degradation. A slight excess of CH_3Cl is used to assure virtually complete conversion of the sodium arsenite. Schanhals (1967)[2] contends that the preferred pressure is 175 psig.

Following the addition of all reactants, the contents are allowed to "digest" until the reaction ceases, during which time the pressure drops to 5 to 10 psig. The reaction medium can also contain small amounts of catalysts or promoters, for example, a mixture of a saturated aliphatic ketone with high-boiling mineral spirits.

Following digestion, the medium is allowed to cool, and the DSMA is precipitated and filtered. Precipitation is augmented by the addition of a suitable liquid, such as isopropyl alcohol.

Yields through the DSMA reaction may be 97% or more based upon As_2O_3. With proper digestion, residual inorganic arsenic (as As_2O_3) is under 0.8% (Urbanowski and Steinkoenig 1969).

Most of the sodium chloride and sodium sulfate remain in solution. Stoichiometrically, 36.1 lb of NaCl and 43.8 lb of Na_2SO_4 would be produced per 100 lb of MSMA. But according to Schwerdle (1959) the NaCl and Na_2SO_4 are simply diluents which do not affect the herbicidal properties.

DSMA may also be produced with methyl iodide, CH_3I, or methyl sulfate, $(CH_3)_2SO_4$, as the methylating agent (Schwerdle 1959).

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[1] Urbanowski, R. L., and R. P. Steinkoenig (to Diamond Shamrock Corporation), U.S. Patent No. 3,440,258 (22 April 1969).

[2] Schanhals, L. R. (to O. M. Scott & Sons), "Process for the Manufacture of Lower Alkyl Arsinic Acids and Alkali Metal Salts Thereof," U.S. Patent No. 3,322,805 (1967).

Physical Properties

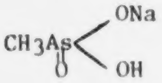
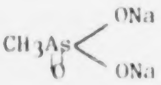
Chemical Name: MSMA, Monosodium methanearsonate
DSMA, Disodium methanearsonate

Common Name: MSMA, DSMA

MSMA Trade Names: Ansar 170 H.C., Ansar 529 H.C., Bueno, Daconate, Phyban H.C., Silvisar 550, Weed-E-Rad, Weed-Hoe.

DSMA Trade Names: Ansar 8100, Ansar DSMA Liquid, Arrhenal, Arsinyl, Chipco Crab Kleen, Crab-E-Rad, Dal-E-Rad 100, Di-Tac, DMA, DMA-100, Methar, Sodar, Weed Broom, Weed-E-Rad, Weed-Hoe.

Pesticide Class: Herbicide; arsenical

	MSMA	DSMA
Empirical Formula:	CH_4AsO_3Na	$CH_3AsO_3Na_2$ (pure) $CH_3AsO_3Na_2 \cdot 6H_2O$ (hexahydrate)
Structural Formula:		
Molecular Weight:	161.94	183.93 (pure) 292.03 (hexahydrate)
Physical State:	White to faint yellow liquid aqueous solution. Odorless (Vineland)	DSMA hexahydrate White, fine crystalline powder. Odorless (Vineland)
Specific Gravity:	1.56 at 20°C (Vineland)*[1]	
Density:	13 lb/gal (Vineland)*	
Bulk Density:		Approximately 63 lb/ft^3 (Vineland)

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* Figures for Vineland MSMA refer to a 51.2% solution of MSMA with 3% sodium chloride.

[1] Vineland Chemical Company, "MSMA-DSMA Weed Control," Vineland, New Jersey (undated).

	MSMA	DSMA
Melting Point:	Below 10°F (Vineland)* 115-119°C (von Rümker et al. 1974)**	132-139°C, slowly decomposes at elevated temperatures (Martin 1971)[1] 132-139°C (Frear 1969)[2]. May sinter if enclosed in its water or crystallization. Decomposes at very high temperature (Vineland).
Boiling Point:	112°C (Vineland)*	
Flammability:	Nonflammable	Nonflammable
Solubility:	57% w/w at 25°C (Ansul 1971)[3] 195.5 g/100 g H_2O at 25° (Vineland)	28% w/w at 25°C (Ansul 1971) 36% w/w at 20°C (Diamond Shamrock 1970)[4]. 25.4% w/w at 25°C (Martin 1971). Very soluble in water. Moderately soluble in low molecular weight alcohol (Frear 1969). Soluble in methanol but practically insoluble in other organic solvents (Martin 1971).
pH:		11.2 (5% solution)(Vineland) 10.5 (no concentration given) (Ansul 1971).
Corrosivity:	Noncorrosive to stainless steel, rubber, alloys and plastics.	Noncorrosive to stainless steel, rubber, alloys and plastics.

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* Figures for Vineland MSMA refer to a 51.2% solution of MSMA with 3% sodium chloride.

** This melting point range is for the 1.5 hydrated form--the anhydrous MSMA decomposes and does not yield a melting point.

[1] Martin, H., Pesticide Manual, British Crop Protection Council, 2nd ed. (1971).

[2] Frear, D. E. H., Pesticide Index, 4th ed., College Science Publishers, State College, Pennsylvania (1969).

[3] The Ansul Company, Comments in Support of Continued Registration of Organic Arsenical Herbicides, Marinette, Wisconsin (31 August 1971).

[4] Diamond Shamrock Chemical Company, DSMA - MSMA Herbicides (bulletin) Cleveland, Ohio (1970).

Analytical Methods

This subsection reviews analytical methods for MSMA and DSMA. The review describes multi-residue methods, residue analyses, and formulation analyses. Information on the sensitivity and selectivity of the methods is also presented.

Information Sources - The primary information sources for the analytical methods are as follows: (1) The Pesticide Analytical Manual (PAM),[1] published by the Food and Drug Administration (FDA), is designed to bring together procedures and methods used by the FDA laboratories to examine food samples for the presence of pesticide residues. PAM is published in 2 volumes. Volume I contains procedures for multi-residue methods (for samples of unknown history which may contain more than one pesticide). Volume II contains analytical methods used for specific pesticide residues and for specific foods. (2) Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC),[2] is a methods manual published about every 5 yr. The reliability of the methods must be demonstrated by a published study showing the reproducibility of the method by professional analysts. Methods and collaborative studies are published in the Journal of the Association of Official Analytical Chemists.

Multi-Residue Methods - There are no multi-residue methods which specifically detect MSMA and DSMA. The residue analyses performed by FDA do not detect MSMA and DSMA as an individual chemical; all forms of arsenic are converted to arsenic trioxide (As_2O_3).

Residue Analysis - The Diamond Shamrock Chemical Company (1970) [3] explains the difficulty in detecting residues of arsenical pesticides as follows:

> Analytical methods which can distinguish residues of specific arsenical compounds in plant materials are not available. Gas chromatography and thin-layer chromatography methods do not have sufficient sensitivity to quantitatively analyze methanearsonate herbicides....In addition, no method is available for extracting DSMA or MSMA from plant tissue without altering the chemical composition of the methanearsonate ion. Therefore, all quantitative analyses of methanearsonate residues employ the total arsenic method.

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[1] U.S. Department of Health, Education, and Welfare, Food and Drug Administration, Pesticide Analytical Manual, 2 vols. (1971).

[2] Association of Official Analytical Chemists, Official Methods of Analysis of the Association of Official Analytical Chemists, 11th ed., Washington, D.C. (1970).

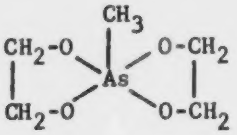
[3] Diamond Shamrock Chemical Company, op. cit. (1970).

There have been some recent developments which may lead to practical, specific methods for the determination of MSMA and DSMA residues.

Sachs et al. (1971)[1] developed a paper chromatographic separation method for cacodylic acid, MSMA, sodium arsenate and sodium arsenite. Four solvent elution systems were employed. Aqueous extraction of plant tissues removed essentially all of the arsenicals applied. The paper chromatographic procedures were followed by colorimetric determinations of the separated arsenicals. The silver diethyldithiocarbamate colorimetric method was useful for detecting as little as 0.6 to 20 μg of arsenic (the color is caused by the formation of an arsine-silver diethyldithiocarbamate complex).

Braman and Foreback (1973)[2] developed a method for analyzing various forms of methylated arsenic acids in the environment at low concentration. This method depends upon reduction of cacodylic acid to dimethylarsine, $(CH_3)_2AsH$, by sodium borohydride at pH 1 to 2. This volatile arsine is then scrubbed out with helium gas and frozen in a liquid nitrogen trap. The arsine gas is then volatilized from the trap and a recording is made of the intensity of arsenic emission lines (234.9 nm or 228.8 nm) produced by an electrical discharge in the carrier gas. The limit of detection is very low, 0.5 ng. Braman and Foreback's method is also applicable to arsenite ion, arsenate ion, and MAA. Since arsine, methylarsine and dimethylarsine will volatilize from the trap in the order of their boiling points, the compounds pass through the detector at different times and the analysis readout is similar in appearance to a gas chromatogram. Thus, the two methylated arsenic acids can be distinguished from one another and from inorganic arsenic. The authors applied this method to the analysis of water samples, bird eggshells, seashells and limestone, and adapted this method to the analysis of urine samples.

MAA can be treated with ethylene glycol to produce a derivative:



1/ Sachs, R. M., J. L. Michael, F. B. Anastasia, and W. A. Wells, "Determination of Arsenical Herbicide Residues in Plant Tissues," *Weed Sci.*, 19(4):412-416 (1971).

2/ Braman, R. S., and C. C. Foreback, "Methylated Forms of Arsenic in the Environment," *Science*, 182(4118):1247-1249 (December 21, 1973).

Johnson et al. (1972)[1] observed that this derivative (which can also be prepared from MSMA or DSMA) produces acceptable peaks when chromatographed on a variety of substrates such as 10% OV-17 on Chromosorb W. Helium or argon was used as a carrier gas; a flame-ionization detector was employed. The minimum detectable amount was 1 ng.

There are, however, specific analytical methods which can distinguish residues of MSMA or DSMA from inorganic arsenicals. The method of Peoples et al. (1971)[2] determines MAA and inorganic arsenic in urine. Methylarsine and arsine are evolved from MAA and inorganic arsenicals, respectively, in a stream of nitrogen, and absorbed in silver diethyldithiocarbamate solution. These compounds absorb at different wavelengths; the absorbances are read and the residues are calculated. The sensitivity is about 0.2 ppm.

Specific residue methods are outlined below:

Gutzeit Method - (Official Final Action) - In the Gutzeit method (AOAC 1970) arsenic (or any arsenic compound) is converted to arsine (a gas) which is allowed to interact with strips of paper treated with mercuric bromide. The amount of arsenic present is determined by the length of the brown color which develops on the strip. The arsine generator apparatus is calibrated using known quantitites of arsenic trioxide (As_2O_3).

Samples of fresh fruits, dried fruit products, vegetables or other materials are treated with nitric and sulfuric acids to convert arsenic compounds to arsenic pentoxide (As_2O_5).

PAM (Vol II 1970) cites the sensitivity of the method as 0.01 to 0.03 mg or about 0.01 ppm. The method, however, has been superceded by colorimetric methods.

Colorimetric Methods - (Official Final Action) - For each of 2 colorimetric methods, the arsenic compound in the sample is converted to arsine (by reduction with zinc) and the arsine is absorbed in a reagent which produces a color (AOAC 1970).

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[1] Johnson, L. D., K. O. Gerhardt, and W. A. Aue, "Determination of Methane Arsonic Acid By Gas-Liquid Chromatography," Sci. Total Environ., 1(1): 108-113 (1972).

[2] Peoples, S. A., J. Lakso, and T. Lais, "Simultaneous Determination of Methyl Arsonic Acid and Inorganic Arsenic in Urine," Proc. West Pharmacol. Soc. 14:178-182 (1971).

Buttrill (1973)[1] described a colorimetric method for determining arsenic residues that has been adopted by AOAC as "official first action" for arsenic in meat and poultry. The method uses the molybdenum blue complex for a spectrophotometric readout and involves ashing with magnesium nitrate at 600°C. Six groups of 4 samples were analyzed. The average recoveries for 0.28 to 2.41 ppm arsenic were 87.6 to 109.3%; the standard deviations ranged from 0.037 to 0.225. The method is based on the work of Kingsley and Schaffert (1951),[2] whose glassware design is used, and on the sample preparation techniques of Evans and Bandemer (1954).[3]

Molybdenum Blue Method - In this method the arsine is absorbed in a solution of ammonium molybdate. The color produced is determined spectrophotometrically (at 845 nm), and is compared to a series of blanks prepared similarly. PAM (Vol II 1970) reports that the molybdenum blue method has a working range between 0.01 and 0.06 ng of arsenic; the sensitivity of the procedure is 0.1 ppm.

Diethyldithiocarbamate Method - With this method, the arsine is absorbed in a solution of silver diethyldithiocarbamate. Potassium iodide and stannous chloride are added, and the color is allowed to develop. The color intensity is determined spectrophotometrically (at 522 nm) and the concentration of arsenic is determined from a standard curve. According to PAM (Vol II 1970), the silver diethyldithiocarbamate procedure has a working range of between 1 and 15 mg of As_2O_3. The sensitivity of the method is estimated to be 0.01 ppm As_2O_3.

Dry Ash Methods - Evans and Bandemer (1954) have demonstrated that biological materials with magnesium nitrate can be ashed in an electric furnace without loss of arsenic. Stone (1967)[4] modified this procedure to enable arsenic analysis in animal tissues at a sensitivity of less than 0.1 ppm.

Hundley and Underwood (1970)[5] investigated a simple, sensitive, and reproducible procedure for the determination of total arsenic in composite food samples. The samples are dry-ashed in the presence of magnesium oxide and magnesium nitrate. Arsenic is then evolved from an acid solution as its hydride. The arsine is reacted with silver diethyldithiocarbamate to give a red complex that is measured spectrophotometrically. The absorbance of this complex is proportional to arsenic over a wide range of concentrations (1 to 20 µg arsenic). The method is sensitive to 0.05 ppm arsenic. The procedure of Hundley and Underwood (1970) utilized the dry-ash procedure of Stone (1967). According to Hundley and Underwood, their method is comparable to the wet-ash procedure and colorimetric determination used as the "official method." However, they note that the official method requires an average of 80 hr for the analysis of the 12 food categories specified in the total diet program while the same number of analyses may be accomplished in 20 to 24 hr using the method of Hundley and Underwood. Furthermore, a substantial improvement in recovery is obtained by this method.

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[1] Buttrill, W. H., "Collaborative Study of Colorimetric Method for Determining Arsenic Residues in Red Meat and Poultry," J. Ass. Offic. Anal. Chem., 56(5):1144-1148 (1973).

[2] Kingsley, G. R., and R. R. Schaffert, "Microdetermination of Arsenic and Its Application to Biological Material," Anal. Chem., 23(6): 914-919 (1951).

[3] Evans, R. J., and S. L. Bandemer, "Determination of Arsenic in Biological Materials," Anal. Chem., 26(3):595-598 (1954).

[4] Stone, L. R., "Note on the Determination of Arsenic in Animal Tissues, Using a Dry Ashing Procedure," J. Ass. Offic. Anal. Chem., 50(6): 1361-1362 (1967).

[5] Hundley, H. K., and J. C. Underwood, "Determination of Total Arsenic in Total Diet Samples," J. Ass. Offic. Anal. Chem., 53(6):1176-1178 (1970).

Atomic Absorption Methods - There have been significant recent developments in the analysis of arsenic by atomic absorption methods. The basis for the new method is the generation of arsine by treatment of the arsenic sample with sodium borohydride. The arsine generated is introduced directly into the flame. The method has been recently described by Thompson and Thomerson (1974)[1/] and by Duncan and Parker (undated).[2/] The method apparently has not yet been used for organo-arsenic pesticides, but it would appear suitable for both formulation and specific residue analyses. The organo-arsenic pesticides would require initial conversion into arsenic oxide by conventional wet digestion or dry-ashing procedures, then by reduction to arsine by aqueous sodium borohydride.

Thompson and Thomerson (1974) report that the detection limit for arsenic is 0.8 mg/ml. In precision studies, these investigators observed that a concentration of 100 ng/ml in 10 separate measurements produced a relative standard deviation of 5.7%.

Duncan and Parker (undated) reported an arsenic sensitivity of 0.1 ng/ml and an absolute sensitivity of 2 ng in the sample used. The authors found that the sample, which was certified by the National Bureau of Standards to contain 14 ± 2 µg/g of arsenic, contained 14.9 ± 0.4 µg/g of arsenic with a relative standard deviation (based on 5 determinations) of 2.6%.

Another atomic absorption method, investigated by Hoover et al. (1974),[3/] is intended for the analysis of food and feed. It has a sensitivity of about

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[1/] Thompson, K. C., and D. R. Thomerson, "Atomic-Absorption Studies on the Determination of Antimony, Arsenic, Bismuth, Germanium, Lead, Selenium, Tellurium and Tin by Utilizing the Generation of Covalent Hydrides," Analyst, 99:595-601 (1974).

[2/] Duncan, L., and C. R. Parker, "Applications of Sodium Borohydride for Atomic Absorption Determination of Volatile Hydrides," Technical Topics, Varian Associates, Palo Alto, California (undated).

[3/] Hoover, W. L., J. R. Melton, P. A. Haward, and J. W. Bassett, Jr., "Atomic Absorption Spectrometric Determination of Arsenic," J. Ass. Offic. Anal. Chem., 57(1):18-21 (1974).

0.05 ppm. A modification of the method, which involves collecting arsine in a plastic bag, has a sensitivity of 0.1 ppm.

Formulation Analysis - Carey (1968)[1] proposed a method for formulation analysis involving a fusion procedure in which the arsonate is decomposed to pentavalent arsenic by a potassium bromate-nitric acid solution. The author tested the method on MSMA (commercial formulation), DSMA and MAA (technical grades), and several other arsenicals. The fusion temperatures preferably are kept below 300°C. Color in the fusion mass indicated interferences, which can be removed by using an ion exchange procedure. Carey (1968) presented actual results for each compound, but did not comment on the overall accuracy of the method.

AOAC (1970) lists 4 methods, with official final action status, for analysis of total arsenic in formulations. However, the methods either specify that they are used for inorganic arsenate or arsenites, or only mention inorganic arsenicals. These methods are the hydrazine sulfate distillation method, the iodometric method, an ion exchange method, and a water-soluble arsenic method.

The Technical Service Division of EPA recommends an iodometric method for the determination of DSMA, which involves an initial conversion of DSMA to As_2O_5 (Bontoyan 1970)[2]. The EPA method is as follows:

> Weigh accurately the sample of approximately 0.25 g into the 500 ml long neck Kjeldahl flask, taking care that none of the sample adheres to the neck of the flask. Cover the sample with 5.5 ml of concentrated H_2SO_4. After sample is dissolved or thoroughly wetted, add 1 to 2 ml of fuming nitric acid. Place on the digestion rack, with the cold finger in place; adjust so that the bottom of the flask is 1 in. above the burner surface. Digest for 55 min. There will be a copious evolution of nitrogen oxides which will escape past the cold finger. If the evolution of these fumes ceases before the end of the digestion period, a few more drops of HNO_3 should be added very cautiously. After 55-min digestion, remove the cold finger and continue digestion to white fumes. Remove flask from heat and cool (to where further additions of chemicals to reaction mixture do not splatter badly). Add 1.5 g ammonium sulfate by funnel directly onto the reaction mixture in bottom of flask. Shake vigorously for 1 min, then cool under cold water tap.

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[1] Carey, W. F., "Determination of Arsenic in Organic Arsonates," J. Ass. Offic. Anal. Chem., 51(6):1300-1301 (1968).

[2] Bontoyan, Warren R., (Technical Services Division, Office of Pesticide Programs, EPA), Personal communication to Dr. Alfred Meiners, Midwest Research Institute, Kansas City, Missouri (November 1970).

Add 60 ml distilled water and 10 ml of KI solution. Place over burner without cold finger and boil until solution is straw-colored (I_2 vapors are evolved). (If boiling is continued too long after proper color is reached, solution will darken again and assay is ruined.)

Remove flask and add sodium thiosulfate solutions, several drops at a time, shaking until the solution is colorless. Have 70 ml water ready and add immediately. Pour this solution into 50 ml of Na_2CO_3 solution contained in a 500-ml Erlenmeyer flask, taking care so as not to lose solution by vigorous evolution of CO_2. Rinse Kjeldahl thoroughly, add to solution in Erlenmeyer flask. Finish neutralizing with Na_2CO_3, add a slight excess. Add starch solution and titrate to a blue end point with standard iodine solution.

Composition and Formulation

MSMA and DSMA are generally sold as aqueous solutions which would contain most of the water-soluble salts and by-products produced in the manufacturing process. Little information is available concerning the kinds and amounts of these materials, but sodium sulfate and sodium chloride are the major constituents. Surfactants are added to many of the formulations, but no information is available concerning the nature of these additives.

The Diamond Shamrock Chemical Company produces methylarsonate herbicides to suit a variety of customer needs. There are 3 basic formulations:

1. DSMA Powder--A dry, crystalline, water-soluble powder suitable for field-mixing with surfactants or manufacturing of wettable powder combination herbicide products.

2. Arsonate Liquid--A concentrated water solution containing 6.6 lb of MSMA/gal which is especially suited for manufacture of premixed MSMA-surfactant formulations or combination herbicide products.

3. MSMA-Surfactant Blends--Diamond Shamrock offers four MSMA-surfactant blends to fit a wide range of usage requirements. Two of these are heavy-duty herbicides.

The Ansul Company also offers a variety of formulations; some representative examples are shown below:

MSMA

Percent	Usage
51.3 (ANSAR 170)	For use in formulating herbicides
47.8 (PHYBAN HC)	Railroad and industrial use
47.8 (ANSAR 529 HC)	Cotton
35.8 (ANSAR 529)	Cotton, Noncrop

DSMA

Percent	Usage
81.0 (ANSAR 8100)	Cotton
21.8 (ANSAR DSMA Liquid)	Cotton, Noncrop

Representative formulations offered by Vineland Chemical Company are shown below:

MSMA

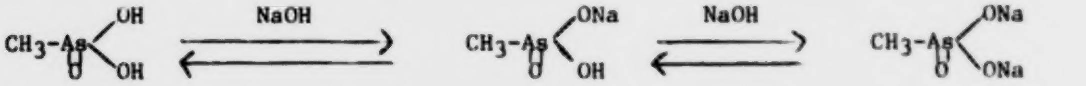
Percent	Usage
44.92	Cotton, general weed control
51.19	Cotton, general weed control
35.33	Cotton, general weed control

DSMA

Percent	Usage
63.00	General weed control, cotton

Chemical Properties and Reactions

Methylarsonic acid (MAA) is a strong acid which forms two sodium salts, monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA).



Methylarsonic acid (MAA) — Monosodium methanearsonate (MSMA) — Disodium methanearsonate (DSMA)

The reaction of MAA with sodium hydroxide (NaOH) first forms the monosubstituted product, MSMA, and then at higher concentrations of NaOH, the disubstituted product, DSMA. Figure 2 is a titration curve of MAA with NaOH. The inflection points at pH 6.5 and 10.5 indicate the formation of MSMA and DSMA, respectively (Vineland Chemical Company undated). Since the reaction is reversible, DSMA will revert to MSMA at pH 6 to 7. DSMA is stable to alkaline hydrolysis (Martin 1971).

MSMA and DSMA are highly stable substances and undergo few chemical reactions. Limited information is available concerning oxidation or reduction reactions, and no information is available concerning the effect of ultraviolet

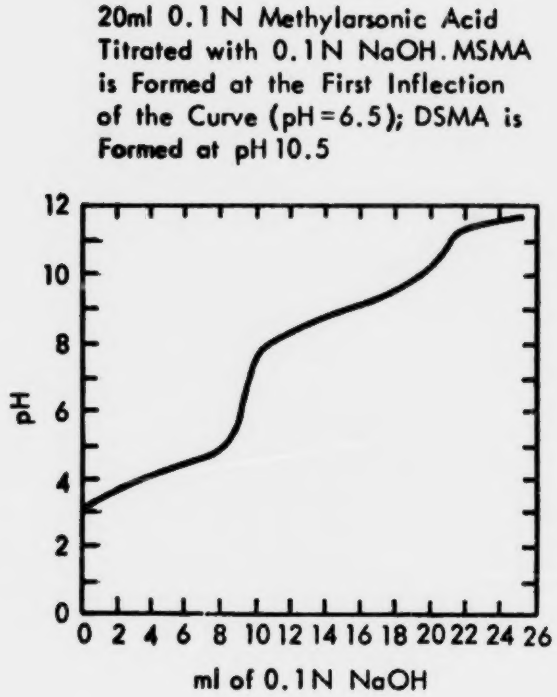
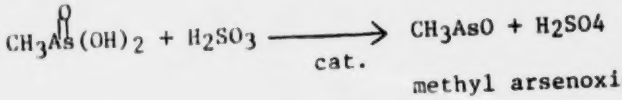


Figure 2. Titration of methylarsonic acid with sodium hydroxide

Source: Vineland Chemical Company, op. cit. (undated).

radiation on these compounds. MAA and its salts are the most stable oxidation state of monomethylated arsenic (Vineland Chemical Company undated). The salts (MSMA and DSMA) cannot be oxidized further except by oxidative degradation of the methyl group. The salts are very resistant to this oxidation (Vineland Chemical Company undated). MAA can be reduced with sulfurous acid. Iodine is useful in this as a catalyst (Melnikov 1971, Noller 1957):[1-2]



$$CH_3\overset{O}{\overset{\|}{As}}(OH)_2 + H_2SO_3 \xrightarrow[\text{cat.}]{} \underset{\text{methyl arsenoxide.}}{CH_3AsO + H_2SO_4}$$

Furthermore, according to Moyerman and Ehman (1965),[3]

$$3CH_3AsO \xrightarrow[\substack{OH^- \\ \text{in air}}]{} As_2O_3 + \underset{\text{trimethylarsine}}{(CH_3)_3As}$$

or $$4CH_3AsO \xrightarrow[\substack{OH^- \\ \text{in air}}]{} \underset{\text{cacodyl oxide}}{(CH_3)_2AsOAs(CH_3)_2} + As_2O_3\ ,$$

if pH is 10.5 or greater.

Anhydrous DSMA is hygroscopic and will become hexahydrated at ambient humidities (Vineland Chemical Company undated). DSMA is sold in the hexahydrated form.

As explained in the Herbicide Handbook (1970)[4] water, high in calcium, magnesium, and iron, tends to precipitate the water-insoluble MAA salts of these ions. Vineland Chemical Company (undated) partially confirms this by stating that ions, such as calcium and magnesium, in concentrated solution, can precipitate the corresponding salts of MAA, which are fairly insoluble. However, they then qualify the statement by saying that calcium methanearsonate is more soluble in cold than hot water. Under normal usage, with even the hardest water in the spray tank, no precipitation may be expected since calcium methanearsonate is water soluble to the extent of about 1,000 ppm at ambient temperatures. Barium, strontium and iron salts are also soluble; magnesium salts have about the same solubility as the calcium salts.

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[1] Melnikov, N. N., Chemistry of Pesticides, Vol. 36 of Residue Rev., 480 pp. (1971).

[2] Noller, C. R., Chemistry of Organic Compounds, 2nd ed., W. B. Saunders Co., Philadelphia, Pa., 978 pp. (1957).

[3] Moyerman, R. M., and P. J. Ehman, (to Ansul Company), "Manufacture of Arsinic Acids," U.S. Patent No. 3,173,937 (1965).

[4] Weed Society of America, Herbicide Handbook, 2nd ed. W. F. Humphrey Press, Inc., Geneva, New York (1970).

DSMA reacts with various salts to form other salts of MAA. The calcium salt, $CH_3AsO_3Ca \cdot H_2O$, is made by warming together a solution of MSMA and calcium chloride. The reaction proceeds according to the following equation:

$$CH_3AsO_3Na_2 + CaCl_2 \xrightarrow{H_2O} CH_3AsO_3Ca \cdot H_2O + 2NaCl$$

The magnesium salt, $CH_3AsO_3Mg \cdot 5H_2O$, is similarly made (Raiziss and Gavron 1923).[1] The silver salt, $CH_3AsO_3Ag_2$, may be prepared by treating MSMA with $AgNO_3$ (Pozzi-Escot 1943).[2]

Alkylation and Dealkylation

Agar cultures of soil bacteria (unspecified), an actinomycete, and a fungus were found to convert 100 ppm ^{14}C-MSMA to arsenate (and CO_2), in an agar culture, to the extent of up to 10% in 3 days and 19% in 7 days (Von Endt et al. 1968).[3] (A more detailed discussion of microbial degradation is presented in the section of this report entitled "Interactions with Lower Terrestrial Organisms.") Noller (1957) reports that chemical elevation may be carried out as:

$$CH_3As(ONa)_2 + (CH_3)_2SO_4 \longrightarrow (CH_3)_2As(O)ONa + CH_3\ NaSO_4$$

Another reaction involves an excess alkylating agent:

$$(CH_3)_2\ AsONa(CH_3)_2\ SO_4 \longrightarrow \underset{\text{trimethylarsine oxide}}{(CH_3)AsO} + CH_3NaSO_4$$

Sachs and Michael (1971)[4] reported that MSMA gave no indication of being demethylated to form inorganic arsenicals, or reduced to trivalent arsenic compounds. DSMA, however, is reported to be decomposed by a strong oxidizing and reducing agent (Martin 1971), but no products were reported. One method of analysis involves digestion of the salts with perchloric acid ($HClO_4$), a strong oxidizing agent, followed by reduction to arsine and colorimetric determination (Johnson and Hiltbold 1969);[5] no specific products were reported.

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[1] Raiziss, G. W., and J. L. Gavron, *Organic Arsenical Compounds*, The Chemical Catalog Company, New York (1923).

[2] Pozzi-Escot, E., "Reaction for the Differentiation of Na Methanearsonate and Na Cacodylate," *Revista de Ciencias* (Peru) 45:379-380 (1943).

[3] Von Endt, D. W., P. C. Kearney, and D. D. Kaufman, "Degradation of Monosodium Methanearsonic Acid by Soil Microorganisms," *Agr. Food Chem.*, 16(1):17-20 (1968).

[4] Sachs, R. M., and J. L. Michael, "Comparative Phytotoxicity Among Four Arsenical Herbicides," *Weed Sci.*, 19(5):558-564 (September 1971).

[5] Johnson, L. R., and A. E. Hiltbold, "Arsenic Content of Soil and Crops Following Use of Methanearsenate Herbicides," *Proc. Soil Sci. Soc. Am.*, 33(2):279-282 (1969).

Occurrence of Residues in Food and Feed Commodities

The FDA, Department of Health, Education, and Welfare, monitors pesticide residues in the nation's food supply through 2 programs. One program, commonly known as the "total diet program," involves the examination of food ready to be eaten. This investigation measures the amount of pesticide chemicals found in a high-consumption varied diet. The samples are collected in retail markets and prepared for consumption before analysis. The other program involves the examination of large numbers of samples, obtained when lots are shipped in interstate commerce, to determine compliance with tolerances. These analyses are complemented by observation and investigations in the growing areas to determine the actual practices being followed in the use of pesticide chemicals.

A majority of the samples collected in these programs are categorized as "objective" samples. Objective samples are those collected where there is no suspicion of excessive residues or misuse of the pesticide chemicals. All samples of imported foods and fish are categorized as "objective" samples even though there may be reason to believe excessive residues may be found on successive lots of these food categories.

Market-basket samples for the total diet studies are purchased from retail stores, bimonthly, in five regions of the United States. A shopping guide with 117 foods for the different regions is used, but not all foods are represented in all regions because of differences in regional dietary patterns. The food items are separated into 12 classes of similar foods (e.g., dairy products; meat, fish and poultry; legume vegetables; and garden fruits) for more reliable analysis and to minimize the dilution factor. Each class in each sample is a "composite." The food items and the proportion of each used in the study were developed in cooperation with the Household Economics Research Division, USDA, and represents the high consumption level of a 16- to 19-year old male. Each sample represents a 2-week supply of food.

Surveillance samples are generally collected at major harvesting and distribution centers throughout the United States and examined in 16 FDA district laboratories. Some samples may be collected in the fields immediately prior to harvest. Surveillance samples are not obtained in retail markets. Samples of imported foods are collected when offered for entry into the United States.

The residue analyses performed by the FDA do not detect MSMA and DSMA as individual chemicals. Residue analyses are made for total arsenic in the form of As_2O_3, but the analytical method does not distinguish between naturally occurring arsenic or arsenic resulting from the presence of any of the arsenical pesticides.

Table 1 presents the results of total diet program for a 6-yr period. The table shows the number of composites which were found to contain arsenic and the concentration ranges (ppm). Although the FDA has continued the analytical program, the results were not published at the time of review.

Table 1. ARSENIC IN TOTAL DIET SAMPLES[a]

Year of study	1[b]	2[c]	3[d]	4[e]	5[f]	6[g]
Date of study[h]	1964-1965	1965-1966	1966-1967	1967-1968	1968-1969	1969-1970
Number of composites	18	28	30	30	30	30
Dairy products	--	--	[i]	[i]	[i]	[i]
Meat, fish and poultry	1 (0.12)	5 (0.1-0.5)	9 (0.1-0.5)	16 (0.1-0.6)	15 (0.1-1.0)	14 (0.1-2.6)
Grain and cereal products	1 (0.10)	1 (0.1)	[i]	5 (0.1-0.8)	7 (0.1-0.2)	--
Potatoes	1 (4.7)	--	--	8 (0.1-0.2)	3 (0.1)	2 (0.1)
Leafy vegetables	--	--	1	6 (0.1-0.3)	4 (0.1)	--
Legume vegetables	1 (0.11)	--	2 (max. 0.18)	1 (0.2)	3 (0.1)	--
Root vegetables	1 (0.10)	1 (0.1)	3 (max. 0.16)	2 (0.1)	3 (0.1)	1 (0.2)
Garden fruits	--	1 (0.1)	--	4 (max. 0.2)	4 (0.1)	1 (0.2)
Fruits	1 (0.18)	--	3 (0.1-0.2)	5 (0.1-0.5)	5 (0.1)	1 (0.2)
Oils, fats and shortening	--	--	2 (0.1)	3 (0.1-0.4)	2 (0.1)	--
Sugar and adjuncts	--	1 (0.1)	4 (max. 0.15)	6 (0.1)	5 (0.1)	--
Beverages	--	--	--	5 (0.1-0.2)	3 (0.1)	--
Totals (concentration ranges, ppm)	6 (0.1-4.7)	10 (0.1-0.5)	33 (0.1-0.4)	65 (0.1-0.8)	57 (0.1-1.0)	21 (0.1-2.6)

---

a/ The values are the number of composites which were found to contain arsenic. The concentration, range or maximum value of arsenic (in ppm) is given in parenthesis. The absence of a value in parenthesis indicates that this information was not available. A dash indicates that none of samples contained arsenic.

b/ Duggan, R. E., H. C. Barry, and L. Y. Johnson, "Pesticide Residues in Total Diet Samples," Sci., 151(3706):101-104 (7 January 1966).

c/ Duggan, R. E., H. C. Barry, and L. Y. Johnson, "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (II)," Pest. Monit. J., 1(2):2-12 (September 1967).

d/ Martin, R. J., and R. E. Duggan, "Pesticide Residues in Total Diet Samples (III)," Pest. Monit. J., 1(4):11-20 (March 1968).

e/ Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (IV)," Pest. Monit. J., 2(4):140-150 (March 1969).

f/ Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (V)," Pest. Monit. J., 4(3):89-104 (December 1970).

g/ Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (VI)," Pest. Monit. J., 5(4):313-329 (March 1972).

h/ June of first year to April of second year, samples taken bimonthly.

i/ Arsenic was stated to be present, but neither the number of composites nor the concentration range was given.

The information in Table 1 was used to calculate the daily intake of arsenic shown in Table 2. Duggan and Corneliussen (1972)[1] drew the following conclusion for the 6-yr period:

> The incidence and levels of As_2O_3 have remained low during the 6 years of this study. While there is a wide variation in the actual annual range, the differences generally are due to higher values for a few samples examined during a particular year. There is a natural low-level background of arsenic in foods, and the values reported during this period are within or slightly above the natural background. The dietary intake of arsenic from pesticide use does not appear to be significant.

Acceptable Daily Intake

The acceptable daily intake (ADI) is defined as the daily intake which, during an entire lifetime, appears to be without appreciable risk on the basis of all known facts at the time of evaluation (Lu 1973).[2] It is expressed in milligrams of the chemical per kilogram of body weight (mg/kg).

The ADI for pesticides is established jointly by the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. However, an ADI for arsenic has not yet been established.

Tolerances

Section 408 of the Food, Drug and Cosmetic Act, as amended, gives procedures for establishing tolerances for pesticide chemicals on raw agricultural commodities. Section 409 applies to food additives, including pesticide chemicals on processed foods. Tolerances for residues of MAA, including MSMA and DSMA, on raw agricultural commodities are cited in the Code of Federal Regulations.[3] They are 0.7 ppm for cottonseed and 0.35 ppm for citrus fruit. Pending tolerances are 0.33 ppm for grapes and 0.39 for sugarcane (U.S. Environmental Protection Agency 1973)[4] Regarding food additive tolerances, a tolerance of 0.9 ppm is established for MAA in or on cottonseed hulls from application of MSMA and DSMA salts of MAA in the production of cotton.[5]

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[1] Duggan, R. E., and P. E. Corneliussen, "Dietary Intake of Pesticide Chemicals in the United States (III), June 1968-April 1970," Pest. Monit. J., 5(4):331-341 (March 1972).

[2] Lu, F. C., "Toxicological Evaluation of Food Additives and Pesticide Residues and Their 'Acceptable Daily Intakes' for Man: The Role of WHO in Conjunction with FAO," Residue Rev., 45:81-93 (1973).

[3] Code of Federal Regulations, Title 40, Chapter 1, Subchapter E, Subpart C, Section 180.289.

[4] U.S. Environmental Protection Agency, EPA Compendium of Registered Pesticides, Vol. I (1973).

[5] Code of Federal Regulations, Title 21, Chapter 1, Subchapter E, Section 561.280.

Table 2. DAILY INTAKE OF ARSENIC RESIDUES[a]

Date of study[b]	1964-1965[c]	1965-1966[c]	1966-1967[d]	1967-1968[d]	1968-1969[e]	1969-1970[e]
Dairy products	--	--	< .001	0.008	0.005	0.006
Meat, fish and poultry	< .001	0.003	0.004	0.045	0.034	0.048
Grains and cereals	0.002	0.001	0.004	0.029	0.011	--
Potatoes	0.063	--	0.003	0.007	0.002	0.001
Leafy vegetables	--	--	0.001	0.002	0.001	--
Legume vegetables	0.001	--	0.001	0.001	0.001	--
Root vegetables	0.001	< .001	0.001	0.001	< .001	< .001
Garden fruits	--	0.001	< .001	0.004	0.001	0.001
Fruits	0.002	--	0.004	0.012	0.004	0.001
Oils, fats and shortening	--	--	0.004	0.002	< .001	--
Sugar and adjuncts	--	0.001	0.001	0.002	0.001	--
Beverages	--	--	0.010	0.024	0.015	--
Total daily intake	--	--	0.033	0.137	0.075	0.057

---

a/ Expressed in milligrams of As_2O_3/day. Includes naturally occurring amounts. A dash indicates that the food class contained no detectable quantities of arsenic.

b/ Samples collected from June of first year to April of second year.

c/ Duggan, R. E., and J. R. Weatherwax, "Dietary Intake of Pesticide Chemicals," Sci., 157:1006-1010 (1 September 1967).

d/ Duggan, R. E., and G. Q. Lipscomb, "Dietary Intake of Pesticide Chemicals in the United States (II), June 1966-April 1968," Pest. Monit. J., 2(4):153-162 (March 1969).

e/ Duggan and Corneliussen, op. cit. (1972).

References

The Ansul Company, Comments in Support of Continued Registration of Organic Arsenical Herbicides, Marinette, Wisconsin (31 August 1971).

Association of Official Analytical Chemists, Official Methods of Analysis of the Association of Official Analytical Chemists, 11th ed., Washington, D.C. (1970).

Bontoyan, Warren R., (Technical Services Division, Office of Pesticide Programs, EPA), Personal communication to Dr. Alfred Meiners, Midwest Research Institute, Kansas City, Missouri (November 1970).

Braman, R. S., and C. C. Foreback, "Methylated Forms of Arsenic in the Environment," Science, 182(4118):1247-1249 (December 21, 1973).

Buttrill, W. H., "Collaborative Study of Colorimetric Method for Determining Arsenic Residues in Red Meat and Poultry," J. Ass. Offic. Anal. Chem., 56(5):1144-1148 (1973).

Carey, W. F., "Determination of Arsenic in Organic Arsonates," J. Ass. Offic. Anal. Chem., 51(6):1300-1301 (1968).

Code of Federal Regulations, Title 40, Chapter 1, Subchapter E, Subpart C, Section 180.289.

Code of Federal Regulations, Title 21, Chapter 1, Subchapter E, Section 561.280.

Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (IV)," Pest. Monit. J., 2(4):140-150 (March 1969).

Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (V)," Pest Monit. J., 4(3):89-104 (December 1970).

Corneliussen, P. E., "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (VI)," Pest. Monit. J. 5(4):313-329 (March 1972).

Diamond Shamrock Corporation, DSMA - MSMA Herbicides (bulletin) Cleveland, Ohio (1970).

Duggan, R. E., H. C. Barry, and L. Y. Johnson, "Pesticide Residues in Total Diet Samples," Sci., 151(3706):101-104 (7 January 1966).

Duggan, R. E., H. C. Barry, and L. Y. Johnson, "Residues in Food and Feed: Pesticide Residues in Total Diet Samples (II), Pest. Monit. J., 1(2):2-12 (September 1967).

Duggan, R. E., and P. E. Corneliussen, "Dietary Intake of Pesticide Chemicals in the United States (III), June 1968-April 1970," Pest. Monit. J., 5(4): 331-341 (March 1972).

Duggan, R. E., and G. Q. Lipscomb, "Dietary Intake of Pesticide Chemicals in the United States (II), June 1966-April 1968," Pest. Monit. J. 2(4):153-162 (March 1969).

Duggan, R. E., and J. R. Weatherwax, "Dietary Intake of Pesticide Chemicals," Sci., 157:1006-1010 (1 September 1967).

Duncan, L., and C. R. Parker, "Applications of Sodium Borohydride for Atomic Absorption Determination of Volatile Hydrides," Technical Topics, Varian Associates, Palo Alto, California (undated).

Evans, R. J., and S. L. Bandemer, "Determination of Arsenic in Biological Materials," Anal. Chem., 26(3):595-598 (1954).

Frear, D. E. H., Pesticide Index, 4th ed., College Science Publishers, State College, Pennsylvania (1969).

Hoover, H. L., J. R. Melton, P. A. Haward, and J. W. Bassett, Jr., "Atomic Absorption Spectrometric Determination of Arsenic," J. Ass. Offic. Anal. Chem., 57(1):18-21 (1974).

Hundley, H. K., and J. C. Underwood, "Determination of Total Arsenic in Total Diet Samples," J. Ass. Offic. Anal. Chem., 53(6):1176-1178 (1970).

Johnson, L. D., K. O. Gerhardt, and W. A. Ave, "Determination of Methane Arsonic Acid by Gas Liquid Chromatography," Sci. Total Environ., 1(1):108-113 (1972).

Johnson, L. R., and A. E. Hiltbold, "Arsenic Content of Soil and Crops Following Use of Methanearsonate Herbicides," Proc. Soil Sci. Soc. Am., 33(2):279-282 (1969).

Kingsley, G. R., and R. R. Schaffert, "Microdetermination of Arsenic and its Application to Biological Material," Anal. Chem., 23(6):914-919 (1951).

Lu, F. C., "Toxicological Evaluation of Food Additives and Pesticide Residues and Their 'Acceptable Daily Intakes' for Man: The Role of WHO, in Conjunction with FAO," Residue Rev., 45:81-93 (1973).

Martin, H., Pesticide Manual, British Crop Protection Council, 2nd ed. (1971).

Martin, R. J., and R. E. Duggan, "Pesticide Residues in Total Diet Samples (III)," Pest. Monit. J., 1(4):11-20 (March 1968).

Melnikov, N. N., Chemistry of Pesticides, Vol. 36 of Residue Rev., 480 pp. (1971).

Meyer, G., Berichte der Deutsche Gesellschaft, Berlin 16:1440 (1883).

Moyerman, R. M., and P. J. Ehman (to Ansul Company), "Manufacture of Arsinic Acids," U.S. Patent No. 3,173,937 (1965).

Noller, C. R., Chemistry of Organic Compounds, 2nd ed., W. B. Saunders Co., Philadelphia, Pa., 978 pp. (1957).

Peoples, S. A., J. Lakso, and T. Lais, "Simultaneous Determination of Methyl Arsonic Acid and Inorganic Arsenic in Urine," Proc. West. Pharmacol. Soc., 14:178-182 (1971).

Pozzi-Escot, E., "Reaction for the Differentiation of Na Methanearsonate and Na Cacodylate," Revista de Ciencias (Peru) 45:379-380 (1943).

Raiziss, G. W., and J. L. Gavron, Organic Arsenical Compounds, The Chemical Catalog Company, New York (1923).

Sachs, R. M., and J. L. Michael, "Comparative Phytotoxicity Among Four Arsenical Herbicides," Weed Sci., 19(5):558-564 (September 1971).

Sachs, R. M., J. L. Michael, F. B. Anastasia, and W. A. Wells, "Determination of Arsenical Herbicide Residues in Plant Tissues," Weed Sci., 19(4):412-416 (1971).

Schanhals, L. R. (to O. M. Scott & Sons), "Process for the Manufacture of Lower Alkyl Arsinic Acids and Alkali Metal Salts Thereof," U.S. Patent No. 3,322,805 (1967).

Schwerdle, A., U.S. Patent No. 2,889,347 (2 June 1959).

Schwerdle, A. (to Vineland Chemical Company), U.S. Patent No. 3,030,199 (17 April 1962a).

Schwerdle, A., (to Vineland Chemical Company), U.S. Patent No. 3,056,821 (2 October 1962b).

Schwerdle, A., (to Vineland Chemical Company), U.S. Patent No. 3,068,088 (11 December 1962c).

Stone, L. R., "Note on the Determination of Arsenic in Animal Tissues, Using a Dry Ashing Procedure," J. Ass. Offic. Anal. Chem., 50(6):1361-1362 (1967).

Thompson, K. C., and D. R. Thomerson, "Atomic-Absorption Studies on the Determination of Antimony Arsenic, Bismuth, Germanium, Lead, Selenium, Tellurium and Tin by Utilizing the Generation of Covalent Hydrides," Analyst, 99:595-601 (1974).

Urbanowski, R. L., and R. P. Steinkoenig (to Diamond Shamrock Chemical Company) U.S. Patent No. 3,440,258 (22 April 1969).

U.S. Department of Health, Education, and Welfare, Food and Drug Administration Pesticide Analytical Manual, 2 vols. (1971).

U.S. Environmental Protection Agency, EPA Compendium of Registered Pesticides, Vol. I (1973).

Vineland Chemical Company, MSMA-DSMA Weed Control, Vineland, New Jersey (undated).

Von Endt, D. W., P. C. Kearney, and D. D. Kaufman, "Degradation of Monosodium Methanearsonic Acid by Soil Micro-organisms," Agr. Food Chem., 16(1):17-20 (1968).

von Rümker, R., E. W. Lawless, and A. F. Meiners, Production Distribution, Use, and Environmental Impact Potential of Selected Pesticides, for Council of Environmental Quality, Contract No. EQC-311 (15 March 1974).

Weed Society of America, Herbicide Handbook, 2nd ed., W. F. Humphrey Press, Inc., Geneva, New York (1970).

PART II. INITIAL SCIENTIFIC REVIEW

SUBPART B. PHARMACOLOGY AND TOXICOLOGY

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This section reviews data on the acute, subacute, and chronic toxicities of MSMA and DSMA and other closely related compounds. Mutagenic effects of MSMA are also considered. Where specific data was not found on MSMA and DSMA metabolic, teratogenic and oncogenic effects, available data on related arsenicals was reported. Studies are also reviewed on occupational and exposure hazards of MSMA and DSMA. This section summarizes rather than interprets data reviewed.

Acute, Subacute and Chronic Toxicity

Toxicity to Laboratory Animals -

Acute Oral Toxicity - Rats - The acute oral toxicity to the rat of Ansar 170, a formulation of MSMA (51.55%), was studied using 120 g Sprague-Dawley albino rats weighing 120 g (Palazzolo 1964a).[1] The rats were divided into 8 groups of 8 animals each (4 males and 4 females). The test animals were intubated with previously determined doses as a 10% aqueous solution. The rats were observed for 14 days. The acute LD_{50} was calculated to be 1.8 g/kg with 95% confidence limits of 1.5 to 2.2 g/kg. The acute oral LD_1 was 0.6 g/kg and the LD_{99} was 5.3 g/kg. Necropsy of animals that died during the study did not reveal any gross pathologic changes in tissues and organs.

A formulation (Ansar 529) containing MSMA (35.21%) was found to have an LD_{50} of 1.8 g/kg to albino rats weighing 120 g. The dead animals exhibited moderate gastroenteritis (Palazzolo 1964c).[2]

The acute oral LD_{50} of DSMA (65.66% DSMA, Ansar 184) to albino rats was calculated to be 2.8 g/kg, with 95% confidence limits of 2.2 to 3.7 g/kg. The animals used in the test were Sprague-Dawley strain albinos of approximately 120 g body weight. The animals were divided into groups of 8 rats each (4 males and 4 females) and were dosed directly into their stomachs with predetermined quantities of test material as a 10% solution. They were observed for 14 days after treatment. Necropsy of those that died during the study showed only moderate to severe gastroenteritis (Palazzolo 1964b).[3]

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[1] Palazzolo, R. J., "Acute Oral Toxicity of Ansar 170," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964a).

[2] Palazzolo, R. J., "Acute Toxicity of Ansar 529 Herbicide," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964c).

[3] Palazzolo, R. J., "Acute Oral Toxicity of Ansar 184 Herbicides," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964b).

The acute oral LD_{50} of MAA, the parent compound of MSMA and DSMA, (98.8%) to albino rats weighing 200 to 300 g was determined using Sprague-Dawley strain animals. The material was administered as an aqueous solution with a dosing syringe. Three levels of test material were used (0.5, 1.0, and 2.0 g/kg) and untreated controls were included. The oral LD_{50} was calculated to be 1.4 g/kg, a value considered by the author to be slightly toxic (Powers 1963).[1]

Acute Inhalation Toxicity - Rats - Inhalation tests (Nees 1969a)[2] were conducted using 10 Sprague-Dawley strain albino rats.

The rats were placed in a 6 cu ft test chamber and exposed to an atmosphere containing an average dose of 11.6 g of Ansar 529. The rats were exposed for 15 min in the chamber followed by an exposure to fresh air for 15 min. The procedure was repeated until a total of 10 successive exposures had been completed. Rats sacrificed immediately after exposure had minimal chronic pneumonitis or bronchitis. Only 1 of the 5 animals sacrificed on the fourteenth day of the observation period had developed moderate chronic bronchitis. No adverse histological effects were noted.

Subacute Toxicity - Rats - The subacute toxicity of MAA (52.3% arsenic) to weanling rats (Sprague-Dawley strain) was determined over a 90-day feeding period (Derse 1968b).[3] The arsenic compound was fed at dietary levels of 3, 15, 30, and 100 ppm. The results of these tests indicated that there were no significant differences between the untreated controls and the animals in any of the treated groups when body weights, food consumption, hematology, urinalysis, organ weights, or gross and histologic observations were compared.

Dermal Toxicity - Rabbits - A dermal toxicity study for Ansar 529 was conducted on 6 adult male rabbits (Nees 1969b).[4] The clipped skin areas of the rabbits were exposed to doses of Ansar 529 for a 24-hr period. The animals were observed for signs of toxicity during the 2 weeks following treatment. The LD_{50} value was found to be between 2 and 4 g/kg.

1/ Powers, M. B., "Methanearsonic Acid--Acute Oral Toxicity; Primary Skin Irritation," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1963).

2/ Nees, Paul O., WARF Institute report (No. 9031917) submitted to The Ansul Company, Marinette, Wisconsin (April 11, 1969a).

3/ Derse, P. H., "Methane Arsonic Acid 90-Day Feeding Study - Rats," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1968b).

4/ Nees, Paul O., WARF Institute report (No. 9031917) submitted to The Ansul Company, Marinette, Wisconsin, (May 15, 1969b).

Eye Irritation - Rabbits - An eye irritation study was conducted using adult albino rabbits of the New Zealand strain. One-tenth of a ml of Ansar 529 was instilled in one eye of each animal; the other untreated eye served as a control. After treatment the material had eye irritation scores of 0.67, 0, and 0 at 24, 48, and 72 hr, respectively, indicating very minimal irritation only at 24 hr (Nees 1969a).

Subacute Toxicity - Dogs - Five-month-old beagle puppies were fed MAA (an equilibrium form of MSMA at low pH) in a 90-day feeding test (Derse 1968a).[1] The arsenic compound was fed at dietary levels of 0, 3, 15, and 30 ppm by supplementing dry commercial dog food. Each treatment group contained 4 female and 4 male animals.

Data on body weight and food consumption appears to indicate that MAA in the diet at the highest level (30 ppm) had little effect on performance of the animals. Statistical analysis confirmed that there was no significance in the differences in body weights between the treated animals and untreated controls. Hematological examination did not reveal any effect of treatment nor did clinical data on kidney and liver function. Organ weights of treated animals were within normal ranges and variations could not be attributed to treatment with the arsenic compound. Histological examinations revealed slight alterations in some tissues, but these occurred randomly in both treated and control animals. Brain, thyroid, parathyroid, heart, liver, gall bladder, kidney, urinary bladder, spleen, pancreas, lung, adrenals, gonads, submaxillary gland, lymph nodes, muscle, stomach, bone, intestine, and mesenteric lymph nodes were examined.

Toxicity to Domestic Animals -

Acute Oral Toxicity - Cattle - Dairy calves with an average body weight of 400 lb were used to determine the acute oral toxicity of Ansar 529 (24.8% MSMA) and Ansar 170 (51.3% MSMA). The LD_{50} for Ansar 529 was calculated to be 250 mg/kg; for Ansar 170 it was calculated to be 230 mg/kg (Varnell 1965).[2]

Subacute Oral Toxicity - Cattle - Two MSMA formulations were used by Dickinson (1972)[3] to determine the toxicity of the herbicide to cattle. One formulation contained 44.9% MSMA and the other contained 59% MSMA, although in both preparations the total arsenic content was reported to be 21%.

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[1] Derse, P. H., "Methane Arsonic Acid 90-Day Feeding Study - Dog," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1968a).

[2] Varnell, T. R., "Acute Toxicity - Dairy Cattle," unpublished report, E. S. Erwin Associates, Inc., Tolleson, Ariz., EPA Pesticide Petition No. 9F0794 (1965).

[3] Dickinson, J. O., "Toxicity of the Arsenical Herbicide Monosodium Acid Methanearsonate in Cattle," Am. J. Vet. Res., 33:1889-1892 (1972).

The materials were administered orally to the test animals in gelatin capsules. Yearling white-faced cattle were used: 2 for controls, 3 for the 44.9% MSMA preparation and 2 with the 59% MSMA preparation.

Of the 5 cattle treated, 4 succumbed to the toxic effects of the compounds after they were given a total dosage of 100 mg of MSMA per kilogram body weight (10 mg/kg/day for 10 days). Arsenic residues as high as 64 ppm were found in the kidney. Toxic nephrosis and hemorrhagic gastritis were observed in all test animals.

In another test, Libke et al. (1971)[1/] reported a combination of herbicides, including 2/3 gal MSMA, was applied to pasture land at a recommended rate of 24 gal/acre. Each liquid oz contained 657 mg MSMA.

Two-year-old crossbred beef heifers (597 lb average body weight) were divided into 4 groups of 3 animals each and pastured on 3-acre lots for 3 weeks. The cattle were turned into the lots within 1 hr of spraying. Group I was placed on pasture sprayed at the recommended level, Group II on pasture sprayed at 4 times the recommended level, and Group III (controls) on untreated pasture. Group IV was confined and fed hay and grain. Using a dosing syringe, one animal was given 14.7 oz of the mixture; another was given 16 oz. The following day the dose was reduced to 8 oz/day. The third animal was treated with 2 oz of the mixture applied to a 225 sq in area of clipped skin. All 3 of the animals in Group IV were treated daily until they died.

The results of this study were summarized by the authors (Libke et al. 1971). They reported no significant adverse effects in the cattle grazing on pasture, even on the pasture which was treated with 4 times the recommended application rate.

In the Group IV animals, the heifer exposed by contact became diarrheic and refused feed for 10 days prior to death. She lost 124 lb during the 23-day exposure period.

One heifer died after a total dose of 78.7 oz (ninth day) and the other after a total of 47.6 oz (fifth day).

Attempts to relate toxicity to the various ingredients in the mixture were not made.

In another test (Varnell undated b),[2/] dietary levels of 40, 80.1 and 240.2 mg of Ansar 529 per kg body weight were fed daily to 2 Holstein calves per dosage group for 7 days. A reduction in feed consumption was observed for all animals, but only one calf at the highest dosage level exhibited the diarrhea

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[1/] Libke, K. G., D. F. Watson, and T. L. Bibb, "Effects of a Brushwood Killer on Cattle," Mod. Vet. Prac., 52:37-40 (1971).

[2/] Varnell, T. R., "One Week Feeding of Ansar 529 and 560 to Calves," E. S. Erwin and Associates, Inc., report submitted to The Ansul Company, Marinette, Wisconsin (undated b).

which is a characteristic symptom of Ansar 529 poisoning. The investigators speculated that calves could consume approximately 5% of the acute lethal dose of Ansar 529 without interfering with their feed consumption.

In a separate test (Varnell undated a),[1] plots of Johnson grass were sprayed with MSMA in the form of Ansar 529 or Ansar 170 at a rate of 6.93 lb MSMA/acre. Holstein dairy calves were confined to these plots for 24 hr; after this exposure they were removed and observed for 2 weeks. No signs of toxicity were observed in the animals other than mild diarrhea which persisted for approximately 2 days.

Another study is considered in the Fate and Significance in the Environment section on the exposure of cattle grazing in forest areas treated with MSMA and other arsenical herbicides.

Subacute Toxicity - Chickens - The subacute toxicity of DSMA in chickens (Rock Cornish) was evaluated by Hamada and Kobayashi (1968).[2] The amount of DSMA added to the diet, starting with day-old chicks, was equivalent to 5 ppm As_2O_5. The quantity of DSMA in the diet was increased so that by the eighth week the chickens were receiving 10 to 15 ppm as As_2O_5 (5 ppm up to 2 weeks, 10 ppm from 2 to 3 weeks, and 15 ppm from 3 to 8 weeks). The presence of DSMA did not result in any signs of toxicity. The treated chickens exhibited statistically significant increases in growth and were found to have achieved a better feed conversion ratio than the untreated controls.

Metabolism

Accumulation and Excretion - Peoples (1964),[4] in an article on inorganic arsenical compounds, reported on toxicity to cows as compared to the toxicity to laboratory animals. The ppm's for tissue concentration of a trivalent arsenic compound in treated rats fed a diet containing 50 ppm arsenic trioxide for 21 days are as follows: blood (125.0), liver (20.0), heart (43.0), kidney (25.0), spleen (60.0), fat (12.0), gastrointestinal tract (15.0), and skin (27.0). The treated guinea pigs had the following ppm's: blood (4.0), liver (1.0), heart (20.0), kidney (1.0), spleen (15.0), fat (0.8), and gastrointestinal tract (2.0). The following are ppm's recorded for the rabbits used in the study: blood (1.5), liver (1.0), heart (0.2), kidney (1.5), spleen (0.2), fat (0.2), gastrointestinal tract (1.5), and skin (2.5). The ppm's for hamsters are as follows: blood (2.5), liver (15.0), heart (7.0), kidney (5.0), spleen (2.0), fat (0.7), gastrointestinal tract (30.0), and skin (38.0). When fed a control diet, some animals, especially rats, still had measurable levels of arsenic in various tissues.

1/ Varnell, T. R., "Johnsongrass Treated with High Levels of Ansar 529 and 170," E. S. Erwin and Associates, Inc., report to The Ansul Company, Marinette, Wisconsin (undated a).

2/ Hamada, S., and K. Kobayashi, "Studies on the Influence of Arsenicals on the Growth of the Domestic Fowl (Part I) Effect of Methane Arsonic Acid," J. Jap. Soc. Food and Nutr., 21:64-66 (1968).

3/ Peoples, S. A., "Arsenic Toxicity in Cattle," Annal. N. Y. Acad. Sci., 111:644-649 (1964).

In tests on cows, a pentavalent compound was excreted rapidly in the urine. Consequently, there was little storage in tissues, and the residues that were present were rapidly depleted in a feed-off period. Therefore, the arsenic levels that occurred represented "transit" rather than true storage. In tests with 2 other arsenic compounds, arsenic was not excreted in the milk of the cows.

According to Peoples (1964), the rat is unique among the various laboratory animals in its propensity to accumulate arsenic residues, although its sensitivity to the toxic effects of arsenic is comparable to other animals. Accumulation of large amounts of arsenic in the rat was especially noticeable in the blood levels.

Similar studies have shown that chickens fed either trivalent or pentavalent arsenical compounds do not accumulate arsenic in eggs or in tissues (Peoples 1971).[1]

Compound Valence vs. Excretion - Schreiber and Brouwer (1964)[2] studied the relationship of arsenic valence to metabolism and toxicity in the rat. They reported that from 21 to 64% of 2 pentavalent arsenicals were excreted by rats, predominately in the urine. Under identical test conditions, only 9 to 24% of a trivalent arsenical compound was excreted and this was excreted primarily in bile. No valence pattern was noted for arsenic residues in the heart, red blood cells and (nonfasted) spleen.

Utilization of Tissue-Bound Arsenic - A study by Winkler (1962)[3] concluded that trivalent inorganic arsenic is largely changed to the pentavalent form in the rat. Pentavalent arsenic is not reduced.

Coulson et al. (1935)[4] reported that, when rats were fed shrimp-supplemented diets which contained high levels of arsenic (17.7 mg/kg) for 1 year, only a very small amount (2.82 mg/kg tissue) of the arsenic obtained from the shrimp was stored in the liver of the rat. When inorganic arsenic was fed at the same level, arsenic accumulated to 55 to 65 times normal concentration in the body tissues and over 100 times normal concentration (49.1 mg/kg) in livers.

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[1] Peoples, S. A., "Health Aspects of Arsenic Herbicides," in Proc. 23rd Annual Calif. Weed Conf., pp. 115-116 (1971).

[2] Schreiber, M., and E. A. Brouwer, "Metabolism and Toxicity of Arsenicals. I. Excretion and Distribution Patterns in Rats," Abstract 589, in Fedn. Proc., 23:199 (1964).

[3] Winkler, W. O., "Identification and Estimation of the Arsenic Residue in Liver of Rats Ingesting Arsenicals, J. Ass. Offic. Anal. Chem. 45:80-91 (1962).

[4] Coulson, E. J., R. E. Remington, and K. M. Lynch, "Metabolism in the Rat of the Naturally Occurring Arsenic of Shrimp as Compared with Arsenic Trioxide," J. of Nutr., 10:255-270 (1935).

During the first 3 months of feeding, 18% of the inorganic arsenic was stored in the bodies of the rats, while only 0.7% of arsenic from shrimp-supplemented diets was stored. The total quantity stored within the first 3 months was not significantly increased by feeding for an additional 9 months.

Rats fed arsenic from shrimp-supplemented diets for 12 months did not exhibit any evidence of toxicity in their growth, physical appearance or activity. Arsenic which occurs in shrimp is apparently bound in an organic complex and, as such, cannot be liberated in the rat.

In tests with another compound on pigs (Winkler 1962), livers from the treated animals contained 5.85 ppm (range 3.9 to 8.4 ppm) arsenic, compared to 0.1 ppm from livers of control pigs. Acetone powders were then made from the livers and these were fed to rats at a level of 30% of the diet. The daily feces and urine collections were analyzed for total arsenic. The average value for 4 rats fed on the acetone powders indicated that all of the organic arsenic compounds were eliminated in the urine and feces; however, only 51% of the inorganic arsenic was recovered during the 7-day test.

The results of this study parallel those of Coulson et al. (1935) in that they appear to show metabolic inertness of tissue-bound arsenic. The results seem to indicate that food chain magnification of arsenicals does not occur.

Teratogenic Effects

Specific data on the teratogenic effects of MSMA and DSMA on mammals was not found. However, one study indicated that sodium arsenate is teratogenic to golden hamsters (Ferm et al. 1971).1/ Arsenic acid (the free acid equivalent of sodium arsenate) is one of the probable terminal degradation products of MSMA and DSMA.

On the eighth day of gestation, pregnant female hamsters were injected intraveneously with sodium arsenate (15 and 25 mg/kg body weight). Control animals were injected with demineralized water. The animals were killed and examined on the 15th day of gestation. Determinations were made of the number of embryos and the number of resorptions (Ferm et al. 1971).

Sodium arsenate affected both resorption and malformation in the hamster; the rates increased with increasing concentration. Malformations of the cranium were the most common developmental anomaly found. The authors concluded that arsenic has a profound effect upon reproduction in the golden hamster and that other animals might be more or less sensitive.

1/ Ferm, V. H., A. Saxon, and B. M. Smith, "The Teratogenic Profile of Sodium Arsenate in the Golden Hamster, Arch. Environ. Health, 22:557-560 (1971).

Mutagenic Effects

MSMA was one of several herbicides evaluated for an ability to induce point mutations in one or more of 4 different microbial systems. The mutagenic rates of MSMA-treated organisms did not differ from spontaneous rates (Anderson et al. 1972).[1]

Oncogenic Effects

There are no reported studies on the oncogenic effects of MSMA and DSMA in animals. A few studies with mice and rats have been reported in which the oncogenicity of inorganic arsenicals was considered. However, studies of the oncogenic effects of inorganic arsenicals on animals and humans are beyond the scope of this review.

Effects on Humans

Two studies were reported concerning the occupational hazards associated with MSMA and DSMA. One of these was related to a field exposure and the other to a hazard arising out of the manufacturing process.

Manufacturing Exposure - DePalma (1969)[2] reported the following case histories which indicate the danger to which workers in plants manufacturing MSMA and DSMA may be inadvertently exposed.

MSMA was being synthesized in a plant by reacting methyl chloride with sodium arsenite. The reaction took place under pressure in a closed, 10 by 12 ft, 600 gal stainless steel tank. Because of a mechanical failure in the apparatus, the operation was stopped before the reaction was completed. The tank was drained, but a solid residue was left on the floor. An aluminum ladder was then placed in the tank to enable the workers to repair the mechanism.

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[1] Anderson, K. J., E. G. Leighty, and M. T. Takahashi, "Evaluation of Herbicides for Possible Mutagenic Properties," J. Agr. Food Chem., 20:649-656 (1972).

[2] DePalma, A. G., "Arsine Intoxication in a Chemical Plant," J. Occup. Med., 11:582-587 (1969).

With the aluminum ladder in the vat, the necessary ingredients for the evolution of arsine gas (AsH_3) were present: (1) arsenic, (2) water and/or acid, and (3) aluminum or another base metal such as zinc or tin.

Five men were exposed to the arsine gas during the repair work. The first 2 men entered the vat, inspected the mixer briefly and exited without experiencing any ill effects.

Approximately 30 min later another man entered the tank without wearing a mask or respirator. He noticed gas bubbling at the foot of the ladder. He felt a chill immediately which was later followed by a burning sensation throughout his body. When the symptoms persisted, he was hospitalized the following day. He was discharged from the hospital 44 days after exposure still suffering from anemia and peripheral neuropathy.

A fourth worker entered the tank without a mask or respirator and remained for approximately 3 min. He removed a sample of the dark, tarry substance at the foot of the ladder. Several hours later he noticed his urine was a dark orange color. He experienced chills, nausea, vomiting, and malaise and was hospitalized the following day.

A fifth worker was exposed to the substance while cleaning the tank. At the same time, steam was piped up through the main drain in the center of the tank in order to melt the solid material. The hose operator was in contact with the rising steam for approximately 15 min. Within 30 min he noticed his urine was unusually dark. He later developed hot and cold flashes, abdominal cramps, nausea and vomiting.

Field Exposure - A study was carried out over a 9-week period to determine the potential occupational hazard of MSMA to tree-thinning crews (Tarrant and Allard 1972).[1]

Urine samples were collected from each worker in the test on Monday mornings before work was begun and on the following Friday at the end of the working day. Subjects were chosen so that the effect of 4 different methods used to apply MSMA to trees could be studied.

The method of application did not appear to affect the arsenic level in urine, although, after a week of exposure, the concentration of total arsenic was elevated in all of the workers. The higher levels detected on Friday were in most instances near normal by the following Monday.

The data in Table 3 summarizes the arsenic values observed on Mondays and Fridays for the various application techniques.

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[1] Tarrant, R. F., and J. A. Allard, "Arsenic Levels in Urine of Forest Workers Applying Silvicides," Arch. Environ. Health, 24:277-280 (1972).

Health problems that could be attributed to arsenic poisoning were not encountered in the study group. Arsenic levels did not accumulate and there was no increase in the arsenic levels in the urine after the first week.

Table 3. **EXPOSURE OF TREE THINNING CREWS TO MSMA**

Treatment	Arsenic in urine (ppm) Monday	 Friday
Control (no exposure)	0.04 ± 0.01	0.07 ± 0.03
Injection operator	0.10 ± 0.01	0.36 ± 0.07
Hack-squirt operator	0.07 ± 0.01	0.26 ± 0.05
Injection hatchet operator	0.10 ± 0.01	0.50 ± 0.12

Source: Tarrant and Allard, op. cit. (1972).

References

Anderson, K. J., E. G. Leighty, and M. T. Takahashi, "Evaluation of Herbicides for Possible Mutagenic Properties," J. Agr. Food Chem., 20:649-656 (1972).

Coulson, E. J., R. E. Remington, and K. M. Lynch, "Metabolism in the Rat of the Naturally Occurring Arsenic of Shrimp as Compared With Arsenic Trioxide," J. of Nutr., 10:255-270 (1935).

DePalma, A. G., "Arsine Intoxication in a Chemical Plant," J. Occup. Med., 11:582-587 (1969).

Derse, P. H., "Methane Arsonic Acid 90-Day Feeding Study - Dog," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1968a).

Derse, P. H., "Methane Arsonic Acid 90-Day Feeding Study - Rats," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1968b).

Dickinson, J. O., "Toxicity of the Arsenical Herbicide Monosodium Acid Methanearsonate in Cattle," Am. J. Vet. Res., 33:188901892 (1972).

Ferm, V. H., A. Saxon, and B. M. Smith, "The Teratogenic Profile of Sodium Arsenate in the Golden Hamster," Arch. Environ. Health, 22:557-560 (1971).

Furst, A., and R. T. Haro, "A Survey of Metal Carcinogenesis," Prog. Exp. Tumor Res., 12:102-133 (1969).

Hamada, S., and K. Kobayashi, "Studies on the Influence of Arsenicals on the Growth of the Domestic Fowl (Part I) Effect of Methane Arsonic Acid," J. Jap. Soc. Food and Nutr., 21:64-66 (1968).

Hwang, S. W., and L. S. Schanker, "Absorption of Organic Arsenical Compounds From the Rat Small Intestine," Xenobiotica, 3:351-355 (1973).

Libke, K. G., D. F. Watson, and T. L. Bibb, "Effects of a Brushwood Killer on Cattle," Mod. Vet. Prac., 52:37-40 (1971).

Maycumber, H. C., "Arsenic Residues in Cattle Grazed in Treated Areas," Contained in L. A. Norris (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (unpublished report 1971).

Nees, Paul O., WARF Institute report (No. 9031917) submitted to The Ansul Company, Marinette, Wisconsin (April 11, 1969a).

Nees, Paul O., WARF Institute report (No. 9031917) submitted to The Ansul Company, Marinette, Wisconsin (May 15, 1969b).

Norris, L. A. (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (unpublished report 1971).

Palazzolo, R. J., "Acute Oral Toxicity of Ansar 170," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964a).

Palazzolo, R. J., "Acute Oral Toxicity of Ancar 184 Herbicides," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964b).

Palazzolo, R. J., "Acute Toxicity of Ansar 529 Herbicide," unpublished report, Industrial Bio-Test Laboratories, Northbrook, Illinois, EPA Pesticide Petition No. 9F0794 (1964c).

Peoples, S. A., "Arsenic Toxicity in Cattle," *N. Y. Acad. Sci. Annals*, 111:644-649 (1964).

Peoples, S. A., "Health Aspects of Arsenic Herbicides," *Proc. 23rd Annual Calif. Weed Conf.*, pp. 115-116 (1971).

Powers, M. B., "Methanearsonic Acid--Acute Oral Toxicity; Primary Skin Irritation," unpublished report, WARF Laboratories, Madison, Wisconsin, EPA Pesticide Petition No. 9F0794 (1963).

Schreiber, M., and E. A. Brouwer, "Metabolism and Toxicity of Arsenicals. I. Excretion and Distribution Patterns in Rats," Abstract 589, in *Federation of American Societies for Experimental Biology*, 23:199 (1964).

Tarrant, R. F., and J. A. Allard, "Arsenic Levels in Urine of Forest Workers Applying Silvicides," *Arch. Environ. Health*, 24:277-280 (1972).

Varnell, T. R., "Acute Toxicity - Dairy Cattle," unpublished report, E. S. Erwin Associates, Inc., Tolleson, Arizona, EPA Pesticide Petition No. 9F0794 (1965).

Varnell, T. R., "Johnsongrass Treated with High Levels of Ansar 529 and 170," E. S. Erwin and Associates, Inc., report submitted to The Ansul Company, Marinette, Wisconsin (undated a).

Varnell, T. R., "One Week Feeding on Ansar 529 and 560 to Calves," E. S. Erwin and Associates, Inc., report submitted to The Ansul Company, Marinette, Wisconsin (undated b).

Winkler, W. O., "Identification and Estimation of the Arsenic Residue in Liver of Rats Ingesting Arsenicals," *J. Ass. Offic. Anal. Chem*. 45:80-91 (1962).

PART II. INITIAL SCIENTIFIC REVIEW

SUBPART C. FATE AND SIGNIFICANCE IN THE ENVIRONMENT

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This section contains data on the environmental effects of MSMA and DSMA, including effects on aquatic species, wildlife, and beneficial insects and interactions with lower terrestrial organisms. Residues in soil, water and air are also discussed. The section summarizes rather than interprets data reviewed.

Effects on Aquatic Species

Fish - The data available on the effect of MSMA and DSMA on fish is limited to acute toxicity studies. In laboratory studies 6 species were tested; the number of replicate tests on each species tested was small.

Table 4 shows the low toxicity of MSMA (and DSMA) to fish; the 96-hr LC_{50} ranges from 13.3 to 96.0 ppm, depending on species, test conditions, and the amount of active ingredient in the formulation tested. One report gives a 48-hr LC_{50} of greater than 1,000 ppm (Hughes 1966).[1]

Lower Aquatic Organisms -

Laboratory Studies - The toxicity of MSMA and DSMA to estuarine animals was studied in the mid-1960's at the then existing Bureau of Commercial Fisheries Biological Laboratory at Gulf Breeze, Florida (Miller and Lowe 1966).[2] Test organisms were exposed for 24 or 48 hr to MSMA and DSMA concentrations of 1.0 ppm in natural flowing seawater at temperatures ranging from 15 to 19°C, salinity of 29% parts per thousand. There were no effects from MSMA or DSMA on pink shrimp (*Penaeus duorarum*) after 48 hr exposure, nor on Eastern oyster (*Crassostrea virginica*) after 24 hr exposure. Effects on shrimp were determined by the percentage of the population exhibiting paralysis or loss of equilibrium; effects on oysters were determined by percent decrease in shell deposition.

Sanders (1970)[3] studied the toxicity of a number of herbicides, including MSMA, to freshwater crustaceans. MSMA was one of several herbicides that were not toxic to scud (*Gammarus fasciatus*) after 96 hr exposure at a concentration of 100 ppm.

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[1] Hughes, J. S., Toxicity of Pesticides to Bluegill Sunfish Treated During 1961-1966, report of the Louisiana Wildlife and Fisheries Commission, New Orleans, Louisiana (1966).

[2] Miller, C. W., and J. I. Lowe, "Toxicity of Herbicides to Estuarine Animals," U.S. Bureau of Commercial Fisheries Biological Laboratory, Gulf Breeze, Florida, unpublished report (1966).

[3] Sanders, H. O., "Toxicities of Some Herbicides to Six Species of Freshwater Crustaceans," J. Water Pol. Cont. Fed., 42(8), Part 1:1543-1550 (1970).

Table 4. TOXICITY OF MSMA AND DSMA TO FISH

Species	Herbicide	Concentration of formulation (% AI)*	LC_{50} (ppm) (95% confidence limits)	Exposure (hr)	Reference
Bluegill	MSMA	34.7	49.2 (25.3 - 95.8)	96	a/
(*Lepomis macrochirus*)		34.8	> 1,000	48	b/
Channel catfish (*Ictalurus punctatus*)	MSMA	34.7	26.8 (20.0 - 35.9)	96	a/
Fathead minnow (*Pimephales promelas*)	MSMA	100	13.3 (5.06- 35.8)	96	c/
Goldfish (*Carassius auratus*)	MSMA	100	31.1 (24.4 - 38.8)	96	c/
Longnose killifish (*Fundulus similis*)	DSMA	25.65	No effect at 40.0	48	d/
Rainbow trout (*Salmo gairdneri*)	MSMA	22.6	96.0	96	e/

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* AI = Active ingredient.

a/ Schoettger, R. A., *Annual Progress Report, 1971*, U.S. Department of the Interior, Fish-Pesticide Laboratory, Fish and Wildlife Service, Columbia, Missouri (1971).

b/ Hughes, *op. cit.* (1966).

c/ U.S. Department of Interior, Fish and Wildlife Service, unpublished data from Fish-Pesticide Laboratory, Columbia, Missouri (1968).

d/ Lowe, J. I., unpublished data from Bureau of Commercial Fisheries Biological Laboratory, Gulf Breeze, Florida (1966).

e/ McCann, J. A., (Chemical and Biological Investigation Branch, Office of Pesticide Programs, EPA), "Fish Toxicity Lab Report," EPA Pesticide Petition No. 9F0794 (1969).

Blythe (1973)[1] studied the effects of MSMA on the unicellular green alga (*Chlorella pyrenoidosa*). Autotropic and heterotrophic growth of the organism in the presence of MSMA was determined by counting cell numbers and measuring chlorophyll absorption at different times during the life of a culture. Oxygen evolution in the light and oxygen consumption in the dark at different herbicide levels were also studied. MSMA concentrations ranging from 2.5 to 3,000 ppm were used in growth and respirometer experiments. In almost all of the growth experiments, MSMA resulted in a stimulation above the check level. There was no significant effect of MSMA on oxygen evolution and only a slight effect on oxygen uptake. The average uptake was 56 ml oxygen/100 min, adjusted to 100 mg dry weight. Oxygen uptake was slightly reduced (9%) at an MSMA concentration of 20 ppm. Stimulation of oxygen uptake (18%) was observed at a MSMA dosage of 3,000 ppm.

Cox and Alexander (1973)[2] investigated the production of trimethylarsine gas from various arsenic compounds including monomethylarsonic acid by 3 sewage fungi isolated from raw sewage, for example, *Candida humicola*, *Gliocladium roseum* and *Penicillium* species. Aliquots of raw sewage were added to culture media and exposed to successively higher concentrations of MAA, ranging from 100 to 2,000 μg/ml. The enrichment cultures obtained in this manner were incubated for 1 month at room temperature, and the headspace gas of each incubation bottle was tested for the presence of trimethylarsine by odor analysis and gas chromatography. In addition to MAA, 3 other arsenic compounds were tested in the same manner, each at pH 5, 6, and 7. The typical garlic odor of trimethylarsine was detected in cultures containing MAA at pH 5, but not at pH 6 or 7. In studies with pure cultures of sewage fungi, *C. humicola* produced only small amounts of trimethylarsine from MAA at pH 5, none at pH 7. *G. roseum* produced 2,970 to 3,700 nmoles of trimethylarsine from MAA, with no appreciable effect of pH, while only 10 to 253 nmoles of trimethylarsine were produced under the same conditions from 1 arsenical herbicide; none were produced from the other 2 arsenic compounds tested. The unidentified *Penicillium* species also produced more trimethylarsine gas from MAA than from the other arsenic compounds.

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[1] Blythe, T. O., "Determination and Characterization of the Effects of Fluometuron and MSMA on *Chlorella*," M.S. thesis, University of Arkansas (1973).

[2] Cox, C. P., and M. Alexander, "Production of Trimethylarsine Gas from Various Arsenic Compounds by Three Sewage Fungi," *Bull. Environ. Contam. Toxicol.*, 9(2):84-88 (1973).

Field Studies - Edwards (1973)[1] studied the effects of MSMA on a salt marsh ecosystem in a series of field experiments conducted in 1971 and 1972. During the summer of 1971, 3 by 6 meter plots of a Spartina alterniflora salt marsh were treated with MSMA by foliar application at different rates and frequencies, including 3 applications at 9,000 ppm once weekly for 3 weeks, and 5 applications of 100, 10, and 1 ppm, respectively, once weekly for 5 weeks. Each treatment and the corresponding controls were replicated 4 times. Symptoms of MSMA damage to Spartina observed in the 9,000 and 100 ppm treatments included necrosis of leaf tips and slight curling and necrosis of leaf margins. MSMA applied 5 times at the rate of 100 ppm decreased the dry matter of living Spartina, while 3 applications at the rate of 9,000 ppm did not noticeably affect it. (The author has no explanation for this seeming inconsistency.) None of the treatments significantly affected the density of Spartina shoots, flowering of Spartina, nor the dry matter of dead Spartina. Three MSMA applications at 9,000 ppm reduced the numbers and dry weight of Littorina irrorata, a mollusk associated with Spartina by 45%, but this decrease was not statistically significant because of the large variation in the spatial distribution of the Littorina population in the area.

In 1972 a second set of plots of the same size (3 by 6 m) was established in another area of a similar marsh and treated with MSMA by spray applications once at 90,000 ppm; 30 times (twice each day for 5 consecutive days at monthly intervals for 3 consecutive months) at 10,000, 1,000, 100, and 10 ppm; and by flooding twice daily for 5 consecutive days each month for 3 consecutive months with either 100 or 0 ppm in seawater. The spray treatments were randomized and replicated 4 times. The flooding experiment was duplicated. None of these treatments altered the number of Spartina shoots. Thirty applications of MSMA at 10,000 ppm decreased the standing crop of living Spartina, increased the standing crop of dead Spartina, and reduced the number of flowering shoots. These applications, as well as the single application at 90,000 ppm increased the percent of dead and necrotic tissue on living shoots of Spartina. Thirty applications of MSMA at 10,000 ppm reduced the numbers and dry matter of Littorina by 68%. None of the other spray treatments affected Littorina adversely.

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[1] Edwards, A. C., "The Effects of an Organic Arsenical Herbicide on a Salt Marsh Ecosystem," M.S. thesis, Auburn University, Auburn, Alabama (1973).

Observations from the flooding experiment suggested that flooding with 100 ppm of MSMA in seawater is no more deleterious to Spartina than spraying at the same concentration. Littorina were adversely affected by (unspecified) environmental conditions in the flooding experiments. Their numbers were reduced in the treated as well as the untreated plots. However, Edwards (1973) concluded that the test results were insufficient to assess their significance.

Thirty foliar applications of 10,000 ppm MSMA and 30 flooding applications of 100 ppm MSMA in seawater resulted in arsenic levels of 26 and 28 ppm in Spartina, and of 26 and 33 ppm in the soil. Littorina contained 100 ppm of arsenic after completion of 30 foliar applications of MSMA at 10,000 ppm. This level declined to 11 ppm within 1 month. Upon completion of the 30 floodings with 100 ppm MSMA in seawater, another mollusk, Modiolus demissus, contained 20 ppm of arsenic, and 16 ppm 1 month later. Edwards does not report arsenic residues in Littorina from the flooding tests, nor in Modiolus from spray tests.

The primary objective of the studies was to determine whether MSMA at concentrations which might conceivably be in tide water as a result of runoff from agricultural land could cause damage to a salt marsh ecosystem. Because most organic arsenicals are tightly bound to soil colloids, and since herbicides are greatly diluted in runoff water, it is highly unlikely that concentrations in tide water would even approach 1 ppm, according to Edwards. He concluded that MSMA would have negligible effects on the parameters studied at pollution concentrations and that high rates of application, equal to or above those recommended for noncrop use, would likely have only limited, short-term effects.

Effects on Wildlife

Data on the effects of MSMA and DSMA on wildlife are also limited. Controlled studies have apparently been limited to 2 species.

Laboratory Studies - Subacute toxicity studies were conducted on mallard ducklings and bobwhite quail, using a technical grade MSMA (51.3%). The ducklings were 10- to 15-day-old pen-reared birds that were in good physical condition at the start of the feeding period. The animals were divided as follows: 5 control groups of 10 birds each; 5 toxic groups of 10 birds each which were given a toxic pesticide in the diet at levels of 68 to 464 ppm; and one test group which was fed at a single dietary level of 5,000 ppm MSMA. The MSMA group was fed for 5 days with treated ration and then for 3 days on untreated. The controls received a standard laboratory diet for the 8-day test period. No signs of systemic toxicity or any abnormal behavioral reaction were observed in the MSMA-treated birds. The dietary median lethal concentration (LC_{50}) of MSMA for ducks was determined to be greater than 5,000 ppm (Fletcher 1973a).[1]

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[1] Fletcher, D., "8-Day Dietary LC_{50} Study with Monosodium Acid Menthanearsonate in Mallard Ducklings," unpublished report of Industrial Bio-Test Laboratories, Northbrook, Illinois (1973).

In studies on bobwhite quail, multiple doses of technical grade MSMA (51.3%) were given at dietary levels of 312.5, 625, 1,250, 2,500, and 5,000 ppm. The birds were fed treated ration for 5 days, followed by 3 days of untreated ration. The dietary median lethal concentration (LC_{50}) was calculated to be 3,300 ppm with 95% confidence limits of 1,941 to 5,610 ppm. Necropsy did not reveal any characteristic gross pathology (Fletcher et al. 1973b).[1/]

A formulation containing 81% DSMA was administered to mallard ducks at a level of 10,000 mg/kg of body weight. Both male and female birds were tested. None of the ducks died. All birds were sacrificed, but an examination for gross pathological conditions of tissues failed to detect any abnormalities (Industrial Bio-Test Laboratory 1973a).[2/]

In a similar study, acute oral LD_{50} of DSMA to bobwhite quail was established as 3,160 mg/kg body weight. Gross pathological examination failed to reveal any abnormalities in any organ or tissue as a result of treatment (Industrial Bio-Test Laboratory 1973b).[3/]

Field Studies - Norris (1971)[4/] presented an interim report on comprehensive, cooperative studies among scientists, forest land managers, and several Pacific Northwest organizations on the fate and environmental impact of organic arsenical herbicides including MSMA and DSMA, in the forest environment. The studies were initiated following the death of 8 range cattle in forest areas where organic arsenical herbicides had been used. Arsenic residues had been found in hair and tissue from 4 of the dead cattle.

Schroedel et al. (1971)[5/] studied the effects on wildlife of arsenical herbicides, including MSMA and DSMA, used in forest management. Animals (numbers not specified) were trapped at various intervals after the use of arsenical herbicides, and arsenic residues were determined in specific tissues or whole bodies. More than 400 determinations of arsenic residues were made on samples collected from 3 treatment areas in western Washington, and 4 in eastern Washington.

[1/] Fletcher, D., D. H. Jenkens, and M. L. Keplinger, "8-Day Dietary LC_{50} Study with Monosodium Acid Methanearsonate in Bobwhite Quail," unpublished report of Industrial Bio-Test Laboratories, Northbrook, Illinois (1973).

[2/] Industrial Bio-Test Laboratories, "Acute Oral LD_{50} for Mallard Ducks (Ansar 8100)," unpublished report to The Ansul Company, Inc., Marinette, Wisconsin (1973a).

[3/] Industrial Bio-Test Laboratories, "Acute Oral LD_{50} for Bobwhite Quail (Ansar 8100)," unpublished report to The Ansul Company, Inc., Marinette, Wisconsin (1973b).

[4/] Norris, L. A., ed., "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

[5/] Schroedel T., H. Hartwell, L. Norris, and J. Allard, "Arsenical Silvicide Effects on Wildlife," contained in Norris, op. cit. (1971).

Several species of birds, mountain beaver and porcupines did not contain detectable arsenic residues. A single deer which was recognized by applicators as a long-time resident of one of the treated areas was also collected. Histopathologic examinations on this animal showed no arsenic-induced lesions, and chemical analysis revealed no arsenic residues. Voles, shrews, mice, and chipmunks contained low levels of arsenic shortly after thinning with arsenical herbicides commenced. About 50% of these animals had arsenic residues between 0.5 and 9.8 ppm arsenic between 2 and 30 days following treatment. Most of the residues were less than 5.0 ppm. Few animals (number not specified) that were collected more than 30 days after treatment contained detectable residues. Most ground squirrels that were collected contained arsenic residues similar to those found in voles, shrews, mice, and chipmunks, but one squirrel collected 1 day after treatment contained residues ranging from 17 to 30 ppm arsenic in various body parts. No further details on numbers of animals, types of tissues analyzed, or other study parameters were given.

A total of 11 dead snowshoe hares was found in one treatment area near Colville, Washington, between June of 1970 and February of 1971. High levels of arsenic in tissues from the hares indicated arsenic poisoning, although postmortem degeneration prevented more detailed studies. Most of the dead hares were found within a few hundred yards of "wash areas," locations where crews disposed of remaining herbicide at the end of the working day and where they washed their equipment and hands. The normal procedure was to empty the remaining contents of "squirt cans" and all wash water on the ground. Severe damage to vegetation at these sites suggested high concentrations of the herbicide. When this method of disposal of excess pesticide and wash water was discontinued, no further mortality of hares was observed in this area. Samples of soil, forest floor material and vegetation from the "wash areas" contained high levels of arsenic.

Two hares were collected 2 and 42 days following treatment with arsenical herbicide in another area in eastern Washington. They did not contain detectable arsenic residues. Five other hares collected in western Washington 232 days after treatment contained either extremely low or nondetectable arsenic residues.

In a comparison test, Harr (1971)[1/] studied the effects of a diet containing 50 ppm MSMA on rabbits. This study was still in progress at the time of Norris' report. Early observations indicated a 35% reduction in food intake in rabbits exposed for 14 days. The animals showed considerable intestinal inflammation and congestion, indicating that this level of MSMA produces considerable sublethal chronic toxicity.

In another related study, Maycumber (1971)[2/] evaluated the exposure of cattle grazing in areas treated with arsenical herbicides including MSMA.

[1/] Harr, J. R., "Functional, Histologic, and Residue Effects of MSMA in Rabbits," contained in Norris, _op_. _cit_. (1971).

[2/] Maycumber, H. C., "Arsenic Residues in Cattle Grazed in Treated Areas," contained in Norris, _op_. _cit_. (1971).

Pre- and post-exposure samples of hair were collected from 37 head of adult cattle grazing in 1970 in a forest area treated with an arsenical herbicide which was also the same area where cattle mortality had been observed in 1969. Similar samples were collected from 28 other head of cattle which grazed in another forest area treated with a commercial formulation of MSMA (48.47% purity; 6 lb/gal). There was no cattle mortality reported in either of the 2 test areas. There was a statistically significant (at the 5% level) increase in arsenic concentrations between pre- and post-exposure samples at both sites. There was no significant difference in arsenic levels between the 2 sites in samples collected at a given time.

Two cows from the MSMA-exposed group and one female deer trapped in the test area were sacrificed for examination of tissues for arsenic residues and arsenic-induced lesions. There was no cow mortality in either of the 2 test areas. No arsenic-induced lesions, and no detectable arsenic residues were found in samples of blood, liver, kidney, lungs, heart, muscle, spleen, tongue, brain, paunch content, or udder of the 2 sacrificed cows. The analytical method used was sensitive to arsenic residues as low as 0.2 ppm. Hard tissues (bone, hair, skin) were apparently not analyzed (Maycumber 1971).

As with all pesticides having wildlife dietary toxicity values greater than 500 ppm, registered labels of MSMA- and DSMA-containing pesticides do not carry specific warning or caution statements in regard to wildlife toxicity. They do include the general statement: "Do not feed treated forage to livestock or graze treated areas."

Data from laboratory investigations on the toxicity of methanearsonates to laboratory animals indicates that their acute oral toxicity is relatively low. However, observations from field studies conducted in the Pacific Northwest, as reported by Norris (1971), indicate misuse of these herbicides or careless dumping of excess spray mixture must be avoided.

Effects on Beneficial Insects

In toxicity tests on honeybees (*Apis mellifera*), Atkins et al. (1973)[1/] summarized the effects of a large number of pesticides and other agricultural chemicals. Using a laboratory procedure which primarily measures a pesticide's contact effect, pesticides were applied in dust form to groups of 25 bees per test level, 3 replicates per each of 3 colonies, for a total of 9 replicates per test level. The procedure permits determination of an LD_{50} value for each pesticide in micrograms of chemical per bee.

Both MSMA and DSMA were classified in a category of pesticides considered relatively nontoxic to honeybees. Pesticides in this category, after exposure to honeybees for 48 hr at 80°F and a 65% relative humidity, were found to be nontoxic at equal to or greater than 11 µg/bee. DSMA produced 9.8% bee mortality at the rate of 217.55 µg/bee.

[1/] Atkins, E. L., E. A. Greywood, and R. L. Macdonald, "Toxicity of Pesticides and Other Agricultural Chemicals to Honey Bees," University of California, Agricultural Extension Report M-16, 37 pages (1973).

Moffett et al. (1972)[1] studied the effect of MSMA and several other herbicides on honeybees. About 50 bees were collected, caged in a 2 x 2 x 6 in. wire pen, and fed 60% sucrose syrup and distilled water. The next day dead bees were removed from the cage, and the remaining live bees were sprayed with MSMA in aqueous solution at a rate equivalent to 4 lb in 20 gal/acre. Dead bees were counted daily for 14 days after spraying. Each treatment was replicated 5 times. MSMA was "extremely toxic to sprayed bees." Bee mortality was about 70% 3 days after spraying.

Morton et al. (1972)[2] and Morton and Moffett (1972)[3] studied the toxicity of herbicides, including MSMA and DSMA, fed orally to honeybees. The test herbicides were fed to newly emerged worker honeybees in 60% sucrose syrup at concentrations of 0, 10, 100, and 1,000 ppm by weight. MSMA and DSMA were found to be extremely toxic at 100 and 1,000 ppm by weight concentrations. MAA, MSMA and DSMA were among the most toxic of all compounds tested; toxicity increased with increasing concentration. At the rate of 1,000 ppm by weight, 50% of the test bees were killed in 2.5 days by MSMA; 1.2 days by DSMA; and 1.5 days by MAA.

The findings of Moffett et al. (1972), Morton et al. (1972) and Morton and Moffett (1972) regarding the bee toxicity of MSMA and DSMA appear to be at variance with those of Atkins et al. (1973). Atkins et al. (1973) applied pesticides to honeybees in dust form, whereas Moffett et al. (1972) applied aqueous sprays, and Morton et al. (1972) and Morton and Moffett (1972) applied the herbicides orally in sucrose syrup. MSMA and DSMA appear to be more toxic when applied to honeybees topically in aqueous solution (Moffett et al. 1972) and orally in sucrose syrup (Morton and Moffett 1972) than when applied topically in a dry dust form (Atkins et al. 1973).

Newton and Holt (1971)[4] reported an interesting observation on the mortality of 2 species of Coleoptera in Ponderosa pines injected with MSMA and other arsenical herbicides. The 2 insects involved were pests, rather than beneficial insects.

Treatments consisted of MSMA at 6.67 lb AI/gal, applied by injection with a "Hypo-Hatchet" tree injector at waist height. A volume of about 1.3 ml of undiluted material was applied in each injection. In the treatment area, the presence of all insects under observation was confirmed in scattered dead or dying trees. For the control, plots were thinned with other treatments, including felling and nonarsenical injection.

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[1] Moffett, J. O., H. L. Morton, and R. H. Macdonald, "Toxicity of Some Herbicidal Sprays to Honey Bees," J. Econ. Entomol., 65(1):32-36 (1972).

[2] Morton, H. L., J. O. Moffett, and R. H. Macdonald, "Toxicity of Herbicides to Newly Emerged Honey Bees," Environ. Entomol., 1(1):102-104 (1972).

[3] Morton, H. L., and J. O. Moffett, "Effects of Herbicides on Honey Bees," Proc. West. Soc. Weed Sci., 25:15-16 (1972).

[4] Newton, M., and H. A. Holt, "Scolytid and Buprestid Mortality in Ponderosa Pines Injected with Organic Arsenicals," J. Econ. Entomol., 64(4):952-958 (1971).

All organic arsenical treatments resulted in lower attack levels on the treated trees than on the control trees by the insects studied, including the mountain pine beetle (Dendroctonus ponderosae) and the pine engraver (Ips pini). No larvae of these species were found alive. There was much evidence of larval mortality and hatch failure. The authors speculate that an endometatoxic reaction involving reduction of the organic arsenicals to arsines may be a possible explanation for the insecticidal effectiveness observed.

However, the controls in the experiment consisted only of untreated felled trees, which beetles preferentially attack, even over dead standing trees (Nagel et al. 1957).[1/]

Interactions with Lower Terrestrial Organisms

Studies on the interactions between arsenicals and microorganisms date back to the early nineteenth century. Gosio, an Italian researcher, stated that certain fungi including Aspergillus glaucus, Aspergillus virens, Mucor mucedo, Mucor ramosus, and Penicillium brevicaule produce a poisonous gas from moldy wallpaper caused by arsenic in the pigment. This gas became known in the literature as "Gosio-gas"; Gosio himself believed it to be an alkyl arsine. Challenger et al. (1933)[2/] and Challenger and Higginbottom (1935)[3/] wer the first to identify "Gosio-gas" correctly as trimethylarsine. They demonstrated that a strain of Penicillium brevicaule added to culture media containing sodium methylarsonate produced trimethylarsine. A large number of experiments was conducted in an effort to classify the mechanism of this biological methylation. Results were inconclusive. In the course of the studies, it was found that three bacterial species, Bacterium mesentericus vulgatis, Bacterium mesentericus ruber, and Bacterium subtilis, did not give off the typical garlic odor of trimethylarsine when added to glucose-meat extracts (at 37°C) that were tested separately with several organic and inorganic arsenical compounds.

More recently, McBride and Wolfe (1971)[4/] showed that cell extracts and whole cells of a strain of Methanobacterium methylate and reduce arsenate to dimethylarsine under anaerobic conditions. These preparations produced dimethylarsine from arsenate, arsenite, and methylarsonic acid. The process involves a series of methylations and reductions and requires adenosine triphosphate, hydrogen, and a methyl donor (^{14}C-methylcobalamin). In the pathway, arsenate is reduced to arsenite which is methylated to form MAA. Dimethylarsinic acid, formed by the reductive methylation of MAA, is reduced

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[1/] Nagel, R. H., D. McComb, and F. B. Knight, "Trap Tree Method for Controlling the Engelmann Spruce Beetle in Colorado," J. Forestry, 55(12):894-898 (1957).

[2/] Challenger, F., C. Higginbottom, and L. Ellis, "The Formation of Organometalloidal Compounds by Microorganisms, Part 1. Trimethylarsine and Dimethylethylarsine," J. Chem. Soc. Trans., pp. 95-101 (1933).

[3/] Challenger, F., and C. Higginbottom, "The Production of Trimethylarsine by Penicillium brevicaule (Scopulariopsis brevicaulis)," Biochem. J., 29:1757-1778 (1935).

[4/] McBride, B. C., and R. S. Wolfe, "Biosynthesis of Dimethylarsine by Methanobacterium," Biochemistry, 10(23):4312-4317 (1971).

to dimethylarsine. The authors point out that pollution hazards exist when arsenic and its derivatives are introduced into an environment where anaerobic organisms are growing.

Von Endt et al. (1968)[1] studied the degradation of MSMA by soil microorganisms. Four types of soil (Sharkey clay, Hagerstown silty clay loam, Cecil sandy loam, and Dundee silty clay loam) were treated with ^{14}C-labeled MSMA at 10 and 100 ppm. All soils were initially adjusted to field capacity and incubated for 21 to 60 days at 28 to 30°C. Steam-sterilized soils served as controls. Measurement of evolved $^{14}CO_2$ indicated that from 1.7 to 10.0% of the MSMA was degraded in nonsterile soil, as compared to 0.7% in steam-sterilized controls. The rate of CO_2 evolution was proportional to the organic matter content of the soils studied. The authors concluded that soil microorganisms appear to play some role in the decomposition of MSMA. In additional tests, 4 soil microorganisms (1 fungus, 2 actinomycetes, and 1 bacterium not further identified), isolated in pure culture degraded from 3 to 20% of the MSMA to CO_2 when grown in liquid culture containing 10 ppm of MSMA and 1 g/liter of yeast extract. Thin-layer chromatographic analysis (capable of separating MSMA, arsenate, and arsenite) discovered only arsenate and MSMA in extracts from the soil and from the microbial cultures examined. This data supports the assumption that soil microorganisms are at least partly responsible for MSMA degradation in the soil. The authors pointed out that the metabolism of most organic herbicides leads to the formation of less toxic products. By contrast, they reported that the metabolism of DSMA in soils yields the inorganic arsenate, a compound that is 10 to 25 times more toxic than the parent herbicide.

Newton (1971)[2] also studied the microbial degradation of MSMA. In the introduction to his paper, Newton presents an excellent overview of previous work, including a comment on possible sources of errors in the conclusion reached by Von Endt et al. (1968) as reported in the preceding paragraph. Newton points out that the chromatographic techniques used by Von Endt et al. would not have registered the presence of arsines, and that they may have overlooked the possibility that some of the radioactivity may have been lost through volatilization of arsines.

Newton inoculated Czapek-Dox agar containing various levels of arsenicals with molds cultured from wood. Glucose was added as an energy source to some cultures, while others were glucose-free. After 2 weeks incubation, it was observed that cultures supporting colonies of molds and containing glucose were producing the characteristic garlic odor from substrates containing up to 50,000 ppm MSMA. Further tests were then set up to investigate the relationship between the energy source in the substrate and the ability of molds to produce arsine from MSMA at concentrations of 100, 1,000, and 10,000 ppm. Substantial losses of arsenic occurred at all levels of glucose, and at all 3 concentrations of MSMA. These losses occurred through volatilization at temperatures below 70°C. It was concluded that high concentrations of organic arsenicals are subject to attack by molds and perhaps other microorganisms. Arsines appear to be the principal metabolites responsible for escape of arsenic from the cultures. The findings indicate that there may be substantial losses of arsenic through volatilization following applications of organic arsenical herbicides. The author suggests that the role of organic arsenical herbicides as persistent compounds needs to be reexamined.

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[1] Von Endt, D. W., P. C. Kearney, and D. D. Kaufman, "Degradation of Monosodium Methanearsonic Acid by Soil Microorganisms," Agr. Food Chem., 16(1):17-20 (1968).

[2] Newton, M., "Organic Arsenicals: Breakdown in Forest Trees and in Media Containing Energy Sources - A Progress Report," Oregon State University, Corvallis, Oregon, unpublished report, submitted to Environmental Protection Agency (1971).

May (1974)[1] conducted a series of tests to determine if soil microorganisms contribute to the degradation of arsenical herbicides, including MSMA. The test herbicides were added to soil samples collected in 4 areas of the country: California, Alabama, Central Plains of Texas, and the Rio Grande Valley of Texas. MSMA was added to the soil samples at a concentration of about 50 ppm (27.0 ppm of elemental arsenic). One-half of the soil samples were sterilized by autoclaving prior to addition of the herbicides. Finally, all samples were again subdivided, and about 1 g of corn syrup was added to one-half of the samples to evaluate the effect of an energy source. All samples were exposed to sunshine. The weight of each sample was checked periodically, and water was added to bring the sample back to its original weight if a loss had occurred. Periodically, aliquots were analyzed for arsenic residues and evaluated for the microbial population. The isolations indicated that there was no apparent toxicity to the soil microbes due to the presence of the arsenical herbicides. Analysis of soil samples for elemental arsenic after 60 days showed considerable variations.

Stojanovic et al. (1972)[2] studied the biodegradation and the effects on the soil microflora of a number of pesticides, including DSMA, with a view to the disposal of large quantities of pesticides in the soil. A calcareous West Point loam soil was amended with 5 tons/acre of DSMA AI and subsequently incubated for 56 days. The extent of biodegradation was estimated from the quantity of CO_2 evolved during the incubation period. The effects on microbial populations were determined from plate counts of the incubated samples. Based on the rate of CO_2 evolution, DSMA was not appreciably degraded under these conditions; it inhibited the CO_2 evolution rate by about 9% when compared to the control (soil alone). When a DSMA liquid formulation was incubated with soil in the same manner, there was a 23% inhibition of CO_2 evolution compared to the control. In comparison to soil alone, DSMA inhibited bacterial growth, stimulated the growth of *Streptomyces*, and somewhat inhibited the growth of soil fungi. The findings indicate that excessive concentrations of DSMA in edaphic environments are likely to produce shifts in microbial populations and temporarily to favor microorganisms which may overpopulate the soil and thus create a condition which in some respects is comparable to partial sterilization.

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[1] May, K. J., *Microbial Degradation of Organic Arsenicals*, The Ansul Company, Agrichemical Development Center, Weslaco, Texas, Project No. 32531-71208, Report (1974).

[2] Stojanovic, B. J., M. V. Kennedy, and F. L. Shuman, Jr., "Edaphic Aspects of the Disposal of Unused Pesticides, Pesticide Wastes, and Pesticide Containers," *J. Environ. Qual.*, 1(1):54-62 (1972).

Khurana and Singh (1972)[1] investigated the growth response of Curvularia lunata to 11 herbicides in liquid culture. MSMA stimulated the growth of the fungus, whereas several other herbicides caused inhibition.

Laird and Newton (1973)[2] studied the effects of MSMA and other herbicides on invasion of western hemlock by the fungus Fomes annosus. The herbicides were used as chemical thinning agents by waist-high injections into the trees. Six months later, injection wounds of trees treated with MSMA were not infected.

Residues in Soil

Laboratory and Field Studies - The degradation of organoarsenicals in soil is complex. In its fullest sense, degradation is the complete mineralization of the herbicide molecule (Woolson 1974).[3] Arsenic compounds are normal soil components and arsenic contributes about 4 ppm (dry weight) to most plants. Consequently, most plants are not adversely affected until high arsenic concentrations are reached in soils. According to Woolson et al. (1970a),[4] arsenic concentrations of about 250 ppm in the upper 6 in of soil reduced the growth of 4-week-old corn by about 50%. Under these conditions, dry plant material contained about 10 ppm arsenic (dry weight). Generally, the arsenic level required for phytotoxicity is variable, and is influenced by the chemical form of the arsenic residues, soil fertility level, iron and arsenic in the soil, and plant vigor.

The organic portion of organoarsenicals can be metabolized. Metabolism may include reduction in a volatile compound, which then escapes to the air (Woolson 1974).

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[1] Khurana, S.M.P.A., and S. Singh, "Growth Response of Curvularia lunata to Various Herbicides in Liquid Culture, "Chem. Mikrobiol. Technol. Lebensm., 2:63-65 (1972).

[2] Laird, P.P., and M. Newton, "Contrasting Effects of Two Herbicides on Invasion by Fomes annosus in Tree-Injector Wounds on Western Hemlock," Plant Dis. Rep., 57(1):94-96 (1973).

[3] Woolson, E.A., "Organoarsenical Herbicides." Contained in: P.C. Kearney and D.D. Kaufman, eds., Degradation of Herbicides, 2nd ed., Marcel Dekker, Inc., New York, New York, in press (1974).

[4] Woolson, E.A., J.H. Axley, and P.C. Kearney, "Arsenic Research Summary," U.S. Department of Agriculture, Agricultural Research Service, Crops Protection Research Branch, Pesticide Investigations, unpublished report (1970a).

Schweizer (1967a, 1967b)[1,2] studied the toxicity of DSMA soil residues on cotton, rice, soybeans, oats, corn, and wheat. Soils studied included Bosket silt loam (pH 7.9), collected from an undisturbed creek bank, and Dubbs silt loam (pH 6.4) and Sharkey clay (pH 6.3) collected from fallowed fields. The Bosket and Dubbs silt loams were low-phosphorus soils, the Sharkey clay a high-phosphorus soil. Growth of cotton planted immediately after incorporation of DSMA in Bosket silt loam was reduced significantly by DSMA concentrations of 50 to 80 ppm by weight. This phytotoxicity decreased with time, particularly during the first 16 weeks. DSMA incorporated into the same silt loam at 120 ppm by weight did not significantly inhibit the growth of cotton planted 32 weeks later. The addition of phosphorus (40 to 320 ppm by weight) increased the toxicity of DSMA to cotton, while added phosphorus increased cotton growth in the absence of DSMA. This effect of phosphorus on the phytotoxicity of DSMA was much more pronounced in the low-phosphorus than in the high-phosphorus silt loam.

Schweizer also investigated the effect of 50 ppm by weight of DSMA on corn, oats, rice, soybeans, and wheat, when incorporated into the Bosket silt loam. Rice was the most susceptible crop; wheat was the most tolerant. Growth of rice in the DSMA-treated soil was inhibited by 75%; soybeans by 39%; oats by 12%; corn and cotton by 10%; and wheat by 0%. In a further study, the growth of rice planted in Bosket silt loam 4 weeks after treatment was significantly inhibited at concentrations of DSMA of 5 ppm by weight or more. However, in rice planted 12 weeks after treatment, no toxic residues of DSMA from an initial application as high as 50 ppm by weight were detected. There was no effect on the growth of rice planted in the other two soils 4 weeks after application of DSMA at concentrations as high as 100 ppm by weight.

It is noteworthy that in Schweizer's tests, DSMA was thoroughly incorporated into the soil, whereas under field use conditions, the herbicide is applied to the surfaces of target plants and soil.

Johnson and Hiltbold (1969)[3] studied the arsenic content of soil and crops following use of MSMA and DSMA. The distribution of arsenic at different soil depths was determined after 4 years of repeated applications of these herbicides to turf (established common Bermuda grass, Cynodon dactylon) on Chesterfield sandy loam, pH about 5.5. MSMA and DSMA were applied as sprays at the rates of 2, 4, and 8 lb AI/acre four times each summer during the 1962-1965 period. Soil was not disturbed. The Bermuda grass was mowed as needed and clippings removed. Fertilization adequate for good turf growth was maintained, but there was no irrigation. Over

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[1] Schweizer, E. E., Effects of Residues of DSMA in Soils on Cotton, Soybeans, and Cereal Crops, Mississippi State University, Agricultural Experiment Station, State College, Mississippi, Bulletin 736 (1967a).

[2] Schweizer, E. E., "Toxicity of DSMA Soil Residues to Cotton and Rotational Crops," Weeds, 15(1):72-76 (1967b).

[3] Johnson, L. R., and A. E. Hiltbold, "Arsenic Content of Soil and Crops Following Use of Methanearsonate Herbicides," Soil Sci. Soc. Amer. Proc., 33(2):279-282 (1969).

the 4-yr treatment period, the total arsenic applied as MSMA was equivalent to 14.7, 29.4, and 58.7 lb arsenic/acre, respectively. DSMA provided 12.9, 25.8, and 51.6 lb arsenic/acre.

When soil samples were analyzed for arsenic content at the end of this 4-yr treatment regimen, arsenic concentrations were highest in the upper 2 in of soil; they decreased with increasing depth. There was little difference in the soil arsenic content between the methanearsonates at similar application rates. The arsenic content of soils in the check plots was then subtracted from that found in the treated plots to provide an estimate of the distribution of the applied arsenic. Essentially all of the arsenic applied at the rate of 2 lb/acre was accounted for within the upper 12 in of soil. Recovery decreased to about 75% at the 4 lb AI/acre rate, and to about 50% at the 8 lb AI/acre rate. Yields of cotton, soybeans, sorghum, corn, oats, vetch, and crimson clover planted in the treated plots in the fifth year were not affected by any of the organoarsenical treatments.

About 90% of the soil arsenic content occurred in the clay fraction, associated with aluminum. By contrast, most of the soil phosphorus was associated with iron minerals and organic matter. These results indicate a considerable difference between arsenic and phosphorus distribution among chemical and mineral forms in the soil. Arsenic is much more extractable by mild salt solutions, suggesting a greater water solubility and lower extent of adsorption, precipitation, or occlusion. Organic forms of arsenic were not found in appreciable concentrations. The authors attribute the incomplete recoveries of arsenic from the high-rate treatments to removal in the form of residues in harvested crops or leaching below the root zone. Regarding the possible development of arsenic toxicity in soils from the continued use of organoarsenicals, the authors suggest that erosion, leaching, and crop removal probably preclude hazardous accumulations of arsenic in most soils treated with normal rates of methylarsonates for weed control.

Hamilton and Arle (1968)[1/] studied the effects of herbicide residues in irrigated soils in Arizona on crops planted in fields that had been treated the previous year. In field tests at Mesa, Arizona, herbicides were applied to a soil containing 42% sand, 37% silt, and 21% clay, and disk-incorporated. Barley and safflower were planted each winter, and cotton and sorghum each summer for 3 successive years following the original application. DSMA, applied at the unusually high rate of 120 lb AI/acre, had no visible effect on any crop in any year. It was the least phytotoxic of all herbicides studied under these conditions.

Baker et al. (1969),[2/] in field experiments, investigated the effects of organic arsenical herbicides on cotton and on the arsenic content of soils in California, Arizona, and Mississippi. Among the methods of application

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[1/] Hamilton, K. C., and H. F. Arle, "Herbicide Residues in Irrigated Soils," Progr. Agr. in Arizona, 21(2):16-17 (1968).

[2/] Baker, R. S., H. F. Arle, J. H. Miller, and J. T. Holstun, Jr., "Effects of Organic Arsenical Herbicides on Cotton Response and Chemical Residues," Weed Sci., 17(1):37-40 (1969).

studied were 1) application of directed sprays to cover small weeds in the drill row having minimal contact on cotton leaves more than 2 to 3 in above the ground, and 2) the application, by nozzle, of topical sprays which covered the entire cotton plant. MSMA and DSMA were applied at 2 or 3 lb/acre in 2 or 3 applications on different plots. Cotton was highly tolerant to directed applications. Topical applications to young cotton (2 to 4 in high) reduced yields slightly, but topical applications at later stages of growth caused progressively severe yield reductions and delayed maturity. The effect of the treatments on the arsenic contents of soils was relatively small in comparison to naturally occurring arsenic levels.

Lange and Fischer (1971)[1/] investigated the residual characteristics of a number of herbicides including MSMA in California for more than 7 yr at various locations throughout the State, from Tulelake in the north to El Centro in the south. MSMA was studied in one test at the West Side Field Station near Five Points, California. The soil consisted of 2.8% organic matter, 24% sand, 44% silt, and 31% clay. Irrigation and rainfall water over a 12-month period was 69 in. MSMA was applied to the soil surface at the rates of 16, 64, and 256 lb AI/acre, followed by sprinkler irrigation, without incorporation. Four months after application, 6 crops (barley, milo, lettuce, sugar beets, broccoli, tomatoes) were planted and evaluated for symptoms of phytotoxicity. Eight months after treatment, 4 new crops (barley, milo, cotton, and tomatoes) were seeded and allowed to grow for about 1 month. They were then evaluated and burned down. One yr after the initial application, another 6 crops (barley, canary grass, safflower, sugar beets, lettuce, and carrots) were planted and evaluated. MSMA at the unusually high rate of 256 lb/acre was slightly phytotoxic to barley at 4 months, but virtually nonphytotoxic at 8 months. No phytotoxicity to any crop at any time was observed at the 16 and 64 lb/acre rates, nor to crops other than barley at the 256 lb/acre rate.

Sandberg et al. (1973)[2/] studied the effects of 6 annual applications of MSMA on arsenic residues in soil. MSMA was applied near Weslaco, Texas, for 6 consecutive years at the rates of 2.0 and 6.0 lb AI/acre per year. Soil cores were collected at the end of each growing season at 3 different depths ranging from 0 to 18 in. After 6 annual applications, both rates of MSMA resulted in statistically significant buildup of arsenic in the upper 6 in of soil (3.3 to 4.5 ppm arsenic above an average background of 11.0 ppm arsenic). Arsenic residues in the 6- to 12-in soil layer were increased only by the higher rate of MSMA, and the arsenic residue levels at the depths of 12 to 18 in were not affected by any of the MSMA treatments.

During the study period, a total of 4.9 and 16.6 lb of elemental arsenic were applied in the form of MSMA at the 2 treatment levels. These figures

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[1/] Lange, A. H., and B. B. Fischer, Studies of Herbicide Residues and Various Cultural Practices, University of California, Agricultural Extension, MA-35, 16 p. (1971).

[2/] Sandberg, G. R., I. K. Allen, and E. A. Dietz, Jr., Arsenic Residues in Soils Treated with Six Annual Applications of MSMA and Cacodylic Acid (CA), The Ansul Company, Marinette, Wisconsin, Report 73 Wes 8-9-10, Project No. 32532-73312, 82 p. (1973).

were converted to parts per million of arsenic in the soil and added to the measured average background arsenic levels to arrive at the total arsenic level that would be expected in the soil after 6 yr of treatment. For the 2.0 lb/acre MSMA rate, the total added arsenic was 2.4 ppm. When added to the 11.0 ppm background, the total arsenic level should have equaled 13.4 ppm; 13.3 ppm of arsenic were actually found. For the 6.0 lb/acre MSMA treatment series, the calculated level of arsenic was 19.3 ppm; however, 16.1 ppm arsenic were found, a deficient equivalent to 16.5% of the predicted concentration.

Speculating about possible reasons for these deficits, the authors reject leaching losses because throughout the entire 6-year test period, there was no significant accumulation of arsenic residues in the 12- to 18-in soil horizon. Microbial reduction of organic arsenicals to gaseous methyl arsines appears to be a more plausible loss mechanism. They further suggest that the rate of reduction depends on the amount of organic arsenicals applied to the soil; the amount of arsenic "lost" from the soil in this study was proportional to the amount of organic arsenic added. Less than 1% of the added arsenic was not recovered at the lowest rate of arsenic applied, while 28% of the applied arsenic was not recoverable in the plots treated at the highest rate of arsenic. The authors hypothesize that if their assumptions are correct, an equilibrium will eventually be reached in which loss mechanisms would remove arsenic from the soil at the same rate as it is applied. (The question of the fate of the "escaping" quantities of arsenicals was not reported.)

The treatment rates of MSMA selected for this study are equivalent to the recommended, and 3 times the recommended, single treatment dose. Two lb MSMA/acre is the recommended rate for a single application; the 6 lb/acre rate corresponds to the cumulative seasonal dose of 3 separate applications.

In a companion study reported by Raab (1970),[1] MSMA was applied to Texas sandy clay loam plots with an organic matter content of 1.5% near Weslaco, Texas. Treatment rates were 2.0 and 6.0 lb AI/acre annually, and 20 to 60 lb AI/acre applied the first year only. In each case, the herbicide was applied in a water solution directly to the soil surface. On the day of treatment agronomic crops, including corn, sorghum, cotton, soybeans, sugar beets, and wheat were planted. At the appropriate stage of growth, corn and sorghum fodder samples were harvested for forage. The corn, sorghum, seed cotton, soybean, wheat, and sugar beets were harvested at maturity for yields. Samples of all harvested products were analyzed for arsenic residues. The yield of soybeans planted immediately after the highest application rate of MSMA (60 lb/acre) was reduced to about 25% of the untreated control. There were no significant adverse effects on the yields of any of the other crops from any of the single MSMA treatments in the first year, nor from the repeat treatments at the lower 2 rates (2.0 and 6.0 lb AI/acre) the following year.

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[1] Raab, H., MSMA Museum Plots, Ansul Test Station, Weslaco, Texas, The Ansul Company Report, (1970).

In an earlier study reported by Ehman (1967),[1] plots of loamy fine sand in Fairfax, South Carolina, were sprayed in 1964 with DSMA at 15, 50, and 100 lb AI/acre. On the same day, cotton, soybeans, sorghum, and peanuts were planted in these plots. Because of stunting, the initial peanuts had to be replanted one month later. Cotton, soybeans, and sorghum grew normally at the 15 lb/acre rate. There was some stunting at the 2 higher rates. This abated somewhat as the season progressed, especially in the plots treated at 50 lb AI/acre. The same plots, without retreatment, were planted to cotton, soybeans, sorghum, peanuts, oats, corn, and tobacco the following year. There were no apparent adverse effects on these crops from the DSMA treatments applied the previous year.

Norris (1971) summarized the results of extensive studies in the Pacific Northwest in which a number of different investigators participated. The objective of these investigations was to evaluate the behavior and impact of organic arsenical herbicides in the forest environment. One of the tests (Canutt et al. 1971)[2] studied the contribution of single-tree treatment with organic arsenical herbicides (as is customary in commercial thinning practices) to arsenic residues in the forest floor, soil, and vegetation. Five trees of each of 3 timber types were treated with MSMA in line with operational practices. Samples of forest floor material, soil, and vegetation were collected at points one-half, 2 and 4 times the crown radius at 0, 6, and 40 weeks after treatment. Analytical data at the first sampling after treatment indicated a rise in the concentration of arsenic in forest floor material from one treatment area. Most of the remaining analytical values showed only small changes in arsenic content. Norris concluded: "Injection of trees with MSMA increased the arsenic level of forest floor material but not soil collected 6 weeks after treatment."

Dickens and Hiltbold (1967)[3] studied the movement and persistence of methylarsonates in soil, including soil adsorption from solutions of DSMA, effects of soil type and pH on the leaching of surface-applied DSMA, and effects of soil type and added organic matter on the oxidation of methylearsonates. Soils studied included Norfolk loamy sand, Augusta silt loam, Decatur clay loam, and Vaiden clay. Soil pH ranged from 6.0 to 6.2 in the first 3 soils, and was 5.3 in the Vaiden clay. Reference clay minerals that were also studied included montmorillonite, kaolinite, limonite, and vermiculite. Adsorption on the natural soils and on the reference materials was determined at initial DSMA concentrations equivalent to 0 to 25 ppm arsenic. Kaolinite removed much more DSMA from solution than did vermiculite. Different size fractions of Augusta silt loam adsorbed different percentages of DSMA, ranging from 11 and 12% of the DSMA quantity applied for the silt and sand fractions, respectively, to 100% of the applied concentrations for the clay fraction. Adsorption by whole soils was generally related to their clay contents.

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[1] Ehman, P. J., Museum Plots - 1964, 1965, and 1967, The Ansul Company, Marinette, Wisconsin, Report, (1967).

[2] Canutt, P. R., L. Norris, and J. Allard, "Arsenic Residues in Forest Floor, Soil, Vegetation, and Water After Injecting Conifers with MSMA," contained in Norris, op. cit. (1971).

[3] Dickens, R., and A. E. Hiltbold, "Movement and Persistence of Methanearsonates in Soil," Weeds, 15(4):299-304 (1967).

In a leaching study in the laboratory, DSMA was applied to the surface of Norfolk loamy sand and Decatur clay loam in columns 9 in long by 3.8 mm internal diameter at a rate equivalent to 100 lb of DSMA hexahydrate per acre, or 3,287 mg arsenic per column. Leaching with 20 successive 1-in (30 ml) increments of water removed 52% of the applied DSMA from Norfolk loamy sand. Rates of movement of DSMA in this soil did not differ at 3 pH levels (5.5, 6.1, and 6.5). In the Decatur clay loam, about one-half of the applied DSMA remained in the top 1 in of the column, and none was leached below 6 in. These widely differing leaching rates of DSMA in the 2 soils are consistent with their respective adsorption capacities for DSMA.

The rate of DSMA decomposition in the 4 soils mentioned above was determined in an additional laboratory experiment in which treated soil samples were incubated for periods of time during which respiration and release of CO_2 derived from ^{14}C-labeled DSMA were measured. After incubation of the soils containing 210 ppm of the radio-labeled DSMA at 30°C for 30 days, the pattern of evolution of $^{14}CO_2$ from Decatur, Augusta and Vaiden soils was similar to that for total CO_2. At 30 days, 0.7, 1.8 and 5.5% of the DSMA-carbon in the soils, respectively, was evolved as CO_2. In the investigators' opinions, this indicated that the oxidation of DSMA occurred coincidentally with the metabolism of soil organic matter. There was no indication of any adaptive oxidation of DSMA in the soils with time. In the Norfolk loamy sand, there was increased decomposition of DSMA relative to soil organic matter at the end of 30 days, suggesting an adaptation of the microbial population to metabolize DSMA. Decomposition of added ryegrass enhanced this process to the extent that 16% of the methylcarbon was recovered as CO_2. The investigators concluded that DSMA is decomposed under aerobic soil conditions and that the amount of organic matter available for microbial activity has a direct effect on the rate of decomposition.

Hiltbold et al. (1974)[1] investigated the distribution of arsenic in soil profiles after repeated applications of MSMA in field and laboratory experiments.

Field plots were set up at 3 locations in Alabama on level areas of Dothan loamy sand, Hartsells fine sandy loam, and Decatur silt loam. Beginning in 1966, MSMA was applied to these plots as broadcast spray prior to the planting of cotton at the rates of 8.9, 17.8 and 35.6 lb AI/acre annually, corresponding to 2.5, 5, and 10 times normal use rates, for 6 consecutive seasons (1966 to 1971). Cumulative amounts of elemental arsenic applied amounted to 24, 49, and 98 lb/acre at the end of the sixth year. A soil core to a 35 in depth was obtained from each plot and sectioned into 6-in increments for analysis. Residual arsenic from MSMA was obtained as the difference between arsenic contents of treated and control samples. Arsenic occurred throughout the sampling depth of the untreated plots, ranging from 2.4 to 12.6 ppm. Percentage recovery of applied arsenic averaged 67% in Hartsells fine sandy loam; 57% in Decatur silt loam; and 39% in Dothan loamy sand. Essentially all of the arsenic recovered in the soils occurred in the plow layer, with no evidence of leaching into deeper zones.

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[1] Hiltbold, A. E., B. F. Hajek, and G. A. Buchanan, "Distribution of Arsenic in Soil Profiles After Repeated Applications of MSMA," Weed Sci., 22(3):272-275 (1974).

Batch equilibrium and soil column studies in the laboratory indicated that the rate of MSMA movement through the surface horizon would be fastest in Dothan loamy sand and slowest in Decatur silt loam. The arsenic distribution with depth measured in the field samples showed that movement of MSMA was less in Decatur than in the other 2 soils. In all soils, leaching in the field was considerably less than adsorption coefficients for MSMA would predict. The authors suggest that this is probably due to MSMA decomposition yielding an inorganic arsenate of lower mobility than MSMA.

The reports reviewed in this subsection indicate that herbicidally effective concentrations of MSMA and DSMA "disappear" rather rapidly from field soils after application. Microbial activity appears to contribute to this degradation, at least to some extent. Several different chemical reactions seem to be involved. There is some disagreement among different investigators concerning the relative importance of different chemical pathways, including reduction of the methanearsonate molecule to form volatile methyl arsines that escape to the air; formation of inorganic arsenate; formation of insoluble salts; adsorption on soil colloids; and ion exchange reactions within the soil.

A very informative tabular summary on the chemical and biological transformations of arsenicals in soil has been prepared by Woolson (1974).

Leaching of MSMA and DSMA through soil profiles appears to be inversely related to the soil clay content. The data reviewed indicates that under field use conditions, leaching of these herbicides below the plow level is not likely to occur to any appreciable extent, with the possible exception of very sandy soils.

A number of agronomic crops appear to be highly tolerant to MSMA or DSMA residues in the soil, even at concentrations many times higher than those that might result from the use of the contact herbicides in accordance with label directions.

Monitoring Studies - In the 1969 National Soils Monitoring Program for pesticides (Wiersma et al. 1972),[1] 1,729 samples of cropland soils from 43 states, and 199 samples of noncropland soils from 11 states, were collected. All samples were analyzed for arsenic residues by atomic absorption spectrophotometry. The minimum detection limit was 0.1 ppm, and the recovery value for arsenic averaged 70%. Results were corrected for percent recovery. More elemental arsenic than other pesticide residues were found. For example, 1,713 of the 1,726 sites sampled (99.3%) had detectable residues of arsenic, ranging from 0.25 to 107.45 ppm, with a mean level of 6.43 ppm. The authors suggest that most of this arsenic was from natural sources, although agricultural sources cannot be ruled out. In the noncropland soil samples, detectable arsenic residues were found in 195 of 198 sites sampled (98.5%), ranging from 0.33 to 54.17 ppm; the mean level was 5.01 ppm.

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[1] Wiersma, G. B., H. Tai, and P. F. Sand, "Pesticide Residue Levels in Soils, FY 1969-National Soils Monitoring Program," *Pest. Monit. J.*, 6(3):194-201 (1972).

The highest arsenic residues in cropland soil across the United States were found in the New England states and in New York, Pennsylvania, Ohio, Kentucky, Arkansas, and North Dakota. Among these states, only one, Arkansas, is a cotton-growing state. Thus, there were no correlations between high soil residue levels of arsenic and the growing of cotton, the crop that receives by far the greatest share of methanearsonate herbicide applications. In a breakdown of arsenic residues by cropping regions, the mean arsenic residues found in cotton regions were lower than those found in corn or vegetable growing regions, but higher than those found in general farming or small grain farming regions, or regions with predominantly irrigated land. Pesticide use records indicated that MSMA and DSMA were used at fewer than 0.5% of all sites sampled.

In the National Soils Monitoring Program for pesticides in 1970 (Crockett et al. 1970),[1] soil and crop samples were collected from 1,506 cropland sites in 35 states. Pesticide use records indicated that MSMA was used at 13 of 1,346 sites sampled, 0.97% of all sites. DSMA was reportedly used at 6 sites, 0.45% of all 1,346 sites sampled. The mean application rate of DSMA was 2.02 lb AI/acre. Eleven of the 13 reported MSMA uses were on cotton; all of the 6 DSMA uses were on cotton. No analyses of soil or crop samples for arsenic were performed in the 1970 program.

The National Soils Monitoring Program did not collect samples in 1971, but sampling was done in 1972. Data from the 1972 program was not included in this review since results were not available.

Residues in Water

Bartley (1970)[2] reported on the monitoring of 7 canals in the Rio Grande Area for arsenic in irrigation water following treatment of ditchbanks with MSMA. The canals were dewatered prior to the treatment, and the initial water over the treated area was sampled for the first 4 hr and then analyzed for arsenic content. The maximum arsenic concentrations found were 0 ppm in 1 canal, less than 0.01 ppm in 2 canals, 0.01 ppm in 3 canals, and 0.48 ppm in 1 canal.

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[1] Crockett, A. B., G. B. Wiersma, H. Tai, W. G. Mitchell, and P. J. Sand, "National Soils Monitoring Program for Pesticide Residues - FY 1970," U.S. Environmental Protection Agency, Technical Services Division, unpublished manuscript (1970).

[2] Bartley, T. R., "Abstract of Progress Report on Herbicide Monitoring," Proc. West. Soc. Weed Sci., 23:65-66 (1970).

In a study of a Bureau of Reclamation project on the Rio Grande, Salman et al. (1972)[1] analyzed arsenic concentrations in irrigation water following application of MSMA to ditchbanks of irrigation systems while ditches were dewatered or full. Samples of treated and untreated water were collected to determine any increase in arsenic residues in the irrigation water following herbicide applications. The soil irrigated by these waters is estimated to possibly contain anywhere from 1 to 70 ppm of naturally occurring arsenic. MSMA was applied at rates ranging from 2.4 to 5.0 lb AI/acre. Three dewatered laterals were treated by spraying both banks of the dry laterals. One full irrigation system was treated by spraying in a downstream direction during application to both banks and the complete water surface. Two other full irrigation systems were treated by spraying downstream on one bank for about 2 miles and then spraying the other bank upstream for the same distance. Maximum arsenic concentrations found in the first water released through 3 MSMA-treated ditchbank sections of dewatered laterals were 0.54, 0.12, and 0.29 ppm. In all 3 laterals, arsenic concentrations dropped to 0.06 ppm or less within 10 min. The maximum arsenic concentration found in water in the lateral in which the entire water surface along with the 2 banks was sprayed was 0.86 ppm. In the other 2 full laterals in which only the banks, but not the water was treated, maximum arsenic concentration was 0.16 and 0.17 ppm arsenic. In all 3 instances, the arsenic concentration decreased rapidly with time.

Laterals treated while full showed lower maximum arsenic concentration in the water than those treated while dewatered, except the one lateral where the entire water surface was (inadvertently) sprayed. Apparently, a greater dilution of the herbicide is obtained when applied to a full system. Calculations from the data collected indicate that from 0.002 to 0.04 lb of arsenic per acre treatment could reach farmland from a 24-hr, 6-in irrigation.

When MSMA was used for forest thinning, in accordance with commercial thinning practice in the studies reported by Norris (1971), an effort was made to determine if any arsenic would be detectable in stream water collected downstream from treated units (Canutt et al. 1971). Five trees in each of 3 different timber types were treated with MSMA, according to commercial practice, and water samples from a nearby stream were taken periodically at points above and below treated areas. No detectable arsenic residues were found in stream water samples using an analytical technique sensitive to 0.01 ppm of arsenic.

Residues in Air

There is some evidence that methanearsonates may be reduced and methylated to form volatile methylarsines which escape to the air from treated soil surfaces. However, no data was found on the possible presence and fate of such MSMA or DSMA degradation products in air.

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[1] Salman, H. A., T. R. Bartley, and A. D. Summers, Progress Report of Residue Studies on Organic Arsenicals Used for Ditchbank Weed Control, U. S. Department of the Interior, Bureau of Reclamation, Report REC-ERC-72-37, 8 p. (1972).

The Ansul Company (1971)[1] suggested that the degradation of MSMA and DSMA via trimethylarsine is of a low order of magnitude since trimethylarsine is rapidly oxidized in air to a non-volatile, pentavelent arsenical. Trimethylarsine is spontaneously flammable in air.

Newton (1971), based on studies reviewed in the subsection on lower terrestrial organisms, reported the presence of high concentrations of organic arsenicals, especially MAA, which are subject to attack by molds, and perhaps other organisms. According to Newton, "The disappearance of substantial amounts of arsenic during an experiment procedure in which there were no opportunities for loss is conclusive evidence for loss by volatilization." Because the boiling points of the organic arsines are 52.7°C (for trimethylarsine) or lower, and because the other volatile arsenic compounds implicated have boiling points ranging above 150°C, the conclusion is drawn that the arsines are the principal metabolites responsible for escape of arsenic from these cultures (Lange 1956).[2] In consideration of the analogy to Challenger's work (1951),[3] it is likely that trimethylarsine constitutes an important fraction of the lost arsenic.

Bioaccumulation, Biomagnification

Woolson et al. (1974)[4] studied the accumulation of ^{14}C-MSMA in a model micro-ecosystem containing daphnids (*Daphnia magna*), crayfish (*Procambarus* sp.), algae (*Oedogonium cardiacum*), catfish (*Ictalurus punctatus*), 10 kg of soil, and 80 liters of water. Crayfish bioconcentrated MSMA up to tenfold from water containing 1 ppm of MSMA. Homogenized crayfish were fractionated in order to isolate and identify the arsenical compounds present. A single compound (not MSMA) was observed in the MSMA-treated crayfish. Work is in progress to identify these arsenic containing compounds.

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[1] The Ansul Company, "Comments in Support of Continued Registration of Organic Arsenical Herbicides, in Response to the *Federal Register* Arsenic and Lead Notice 36 FR 12079," unpublished report, Marinette, Wisconsin, 55 pages (1971).

[2] Lange, N. A., *Handbook of Chemistry*, Handbook Publishers, Inc., Sandusky, Ohio, 1,969 pages (1956).

[3] Challenger, F., "Biological Methylation," contained in: F. F. Nord (ed.), *Advances in Enzymology*, Vol. 12, pp. 429-491, Interscience Publisher, New York, New York (1951).

[4] Woolson, E. A., P. C. Kearney, A. R. Isensee, W. G. McShane, K. J. Irgolic, and R. A. Zingaro, "Bound Arsenic Fractions in a Crustacean," *American Chemical Soc.*, Division of Pesticide Chemistry, 168th National Meeting, Atlantic City, New Jersey (1974).

However, Isensee et al. (1973)[1] studied the distribution of 2 related organic arsenicals among aquatic organisms in a model ecosystem, including mosquitofish (Gambusia affinis), daphnids (Daphnia magna), snails (Physa sp.), and algae (Oedogonium cardiacum). These organisms were exposed to the arsenicals for 3, 29, 32, and 33 days, respectively. Algae and Daphnia bioaccumulated more arsenicals than did the 2 higher food chain organisms, snails and fish. The amount of arsenicals accumulated indicates that they do not have a high potential to biomagnify in the environment. Daphnia magna concentrated the arsenicals by about 2,000 times the water content at the time of sampling. An increase in the biomass in the system, primarily algae, over 32 days largely accounted for a gradual loss of the test compounds from solution.

These observations indicate that some aquatic organisms can accumulate organic arsenicals to high levels. However, organisms representing the higher links in the food chain (snails and fish) had smaller bioaccumulation ratios than lower link organisms (algae and Daphnia).

Environmental Transport Mechanisms

Woolson (1974) proposed an environmental cycle for arsenic. Major inputs into the system come from air and water pollution and from pesticide usage. Soil is the sink where arsenic ultimately returns. Arsenic reaches man through air, water and food. Ingested arsenic is eliminated and returns to the water or soil portions of the environment. Plants and animals receive arsenic from air or water pollution, from the soil, or from pesticide usage. Arsenic reaching the soil may begin the cycle of chemical transformation, precipitation, and/or uptake once again.

According to McBride and Wolfe(1971), arsenate may be converted to dimethylarsine by a series of reduction and methylation steps in which MAA is an intermediate. Woolson(1974) suggests that the arsines produced are likely oxidized back to MAA or cacodylic acid, or demethylated and returned to the arsenate form in the soil. Methylation as well as demethylation can occur in the soil medium.

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[1] Isensee, A. R., P. C. Kearney, E. A. Woolson, G. E. Jones, and V. P. Williams, "Distribution of Alkyl Arsenicals in Model Ecosystems," Environ. Sci. Technol., 7(9):841-845 (1973).

Braman and Foreback (1973)[1] analyzed environmental samples for arsenate and arsenite ions and methylarsenic acids in nanogram amounts. They detected dimethylarsinic acid and MAA in natural waters, bird eggshells, seashells, and human urine. According to the authors, the continued introduction of arsenic compounds into the environment may eventually result in a general increase in their concentrations in water and air due to the bacterial mobilization of all forms of arsenic. They further emphasized the need for information on the effect of all forms of arsenic and ecological systems.

Woolson et al. (1970b)[2] reported that the organic arsenates have about the same leaching and fixing characteristics in the soil as shown by Dickens and Hiltbold (1967) for inorganic arsenates. Additionally, Von Endt et al. (1968) have shown that MSMA is degraded to the inorganic arsenates so that, ultimately, the behavior and fate of inorganic arsenate is of prime importance, regardless of the source of the arsenic. Woolson et al. (1970b) pointed out that arsenic applications to crops by way of pesticides for insect and weed control and for desiccation may result in arsenic accumulations in the soil that may ultimately build up to levels toxic to plants, as well as to other biota.

Data on the behavior of MSMA and DSMA in soil and water indicates that movement of these compounds from treated land to water by leaching appears to be minimal. Observations from the treatment of irrigation ditchbanks indicate that surface transfer of MSMA residues from treated land areas to water likewise appears to be minimal, probably due to fixation phenomena in plants, soils, and sediments.

MSMA and DSMA residues in the soil do not appear to be persistent, as such. Accumulation of herbicidally effective residue levels of the unchanged herbicides in the soil, therefore, appears unlikely. However, gradual accumulation of arsenic-containing degradation products in treated soils appears to be possible, and very little information seems to be available on the possible magnitude and significance of such arsenic buildup.

1/ Braman, R. S., and C. C. Foreback, "Methylated Forms of Arsenic in the Environment," Sci., 182:1247-1249 (1973).

2/ Woolson, E. A., P. C. Kearney, and J. M. Axley, "Chemical Distribution of Arsenic in Soils," U. S. Department of Agriculture, Agricultural Research Service, Crops Protection Research Branch, Pesticide Investigations, unpublished report (1970b).

References

The Ansul Company, "Comments in Support of Continued Registration of Organic Arsenical Herbicides, in Response to the *Federal Register* Arsenic and Lead Notice 36 FR 12709," unpublished report, 55 pp. (1971).

Atkins, E. L., E. A. Greywood, and R. L. Macdonald, *Toxicity of Pesticides and Other Agricultural Chemicals to Honey Bees*, University of California, Agricultural Extension Report M-16, 37 pp. (1973). .

Baker, R. S., H. F. Arle, J. H. Miller, and J. T. Holstun, Jr., "Effects of Organic Arsenical Herbicides on Cotton Response and Chemical Residues," *Weed Sci.*, 17(1):37-40 (1969).

Bartley, T. R., "Abstract of Progress Report on Herbicide Monitoring," *Proc. West. Soc. Weed Science*, 23:65-66 (1970).

Blythe, T. O., "Determination and Characterization of the Effects of Fluometuron and MSMA on *Chlorella*," M.S. thesis, University of Arkansas, Fayetteville, Arkansas (1973).

Braman, R. S., and C. C. Foreback, "Methylated Forms of Arsenic in the Environment," *Sci.*, 182:1247-1249 (1973).

Canutt, P. R., L. A. Norris, and J. Allard, "Arsenic Residues in Forest Floor, Soil, Vegetation, and Water After Injecting Conifers with MSMA," contained in: L. A. Norris (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

Challenger, F., "Biological Methylation," contained in: F. F. Nord (ed.), *Advances in Enzymology*, Vol. 12, Interscience Publisher, New York, New York (1951).

Challenger, F., and C. Higginbottom, "The Production of Trimethylarsine by *Penicillium brevicaule* (*Scopulariopsis brevicaulis*)," *Biochem. J.*, 29:1757-1778 (1935).

Challenger, F., C. Higginbottom, and L. Ellis, "The Formation of Organo-Metalloidal Compounds by Microorganisms, Part I. Trimethylarsine and Dimethylethylarsine," *J. Chem. Soc. Trans.*, pp. 95-101 (1933).

Cox, D. P., and M. Alexander, "Production of Trimethylarsine Gas from Various Arsenic Compounds by Three Sewage Fungi," *Bull. Environ. Contam. Toxicol.*, 9(2):84-88 (1973).

Crockett, A. B., G. B. Wiersma, H. Tai, W. G. Mitchell, and P. J. Sand, "National Soils Monitoring Program for Pesticide Residues - FY 1970," Technical Services Division, U.S. Environmental Protection Agency, unpublished manuscript (1970).

Dickens, R., and A. E. Hiltbold, "Movement and Persistence of Methanearsonates in Soil," *Weeds*, 15(4):299-304 (1967).

Edwards, A. C., "The Effects of an Organic Arsenical Herbicide on a Salt Marsh Ecosystem," M. S. thesis, Auburn University, Auburn, Alabama (1973).

Ehman, A. C., "Museum Plots - 1964, 1965, and 1967," The Ansul Company, Marinette, Wisconsin, unpublished report (1967).

Fletcher, D., "8-Day Dietary LC_{50} Study with Monosodium Acid Methanearsonate in Mallard Ducklings," unpublished report of Industrial Bio-Test Laboratories, Northbrook, Illinois (1973).

Fletcher, D., D. H. Jenkens, and M. L. Keplinger, "8-Day Dietary LC_{50} Study with Monosodium Acid Methanearsonate in Bobwhite Quail," unpublished report of Industrial Bio-Test Laboratories, Northbrook, Illinois (1973).

Hamilton, K. C., and H. F. Arle, "Herbicide Residues in Irrigated Soils," *Progr. Agr. In Arizona*, 21(2):16-17 (1968).

Harr, J. R., "Functional, Histologic, and Residue Effects of MSMA in Rabbits," contained in: L. A. Norris (ed.), "The Behavior and Impact of Organic Arsenical herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

Hiltbold, A. E., B. F. Hajek, and G. A. Buchanan, "Distribution of Arsenic in Soil Profiles After Repeated Applications of MSMA," *Weed Sci.*, 22(3):272-275 (1974).

Hughes, J. S., *Toxcity of Pesticides to Bluegill Sunfish Treated During 1961-1966*, report of Louisiana Wildlife and Fisheries Commission, New Orlean, Louisiana (1966).

Industrial Bio-Test Laboratories, "Acute Oral LD_{50} for Mallard Ducks (Ansar 8100)," unpublished report to The Ansul Company, Marinette, Wisconsin (1973a).

Industrial Bio-Test Laboratories, "Acute Oral LD_{50} for Bobwhite Quail (Ansar 8100)," unpublished report to The Ansul Company, Marinette, Wisconsin (1973b).

Isensee, A. R., P. C. Kearney, E. A. Woolson, G. E. Jones, V. P. Williams, "Distribution of Alkyl Arsenicals in Model Ecosystem," *Environ. Sci. Technol.*, 7(9):841-845 (1973).

Johnson, L. R., and A. E. Hiltbold, "Arsenic Content of Soil and Crops Following Use of Methanearsonate Herbicides," *Soil Sci. Soc. Amer. Proc.*, 33(2):279-282 (1969).

Khurana, S. M. P. A., and S. Singh, "Growth Response of *Curvularia lunata* to Various Herbicides in Liquid Culture," *Chem. Mikrobiol. Technol. Lebensm.*, 2:63-65 (1972).

Laird, P. P., and M. Newton, "Contrasting Effects of Two Herbicides on Invasion by *Fomes annosus* in Tree-Injector Wounds on Western Hemlock," *Plant Dis. Rep.*, 57(1):94-96 (1973).

Lange, A. H., and B. B. Fischer, *Studies of Herbicide Residues and Various Cultural Practices*, University of California, Agricultural Extension, MA-35, 16 p. (1971).

Lange, N. A., *Handbook of Chemistry*, Handbook Publishers, Inc., Sandusky, Ohio, 1,969 p. (1956).

Lowe, J. I., unpublished data from Bureau of Commercial Fisheries Biological Laboratory, Gulf Breeze, Florida (1966).

May, K. K., "Microbial Degradation of Organic Arsenicals," unpublished report, The Ansul Company, Agrichemical Development Center, Weslaco, Texas, Project No. 32531-71208 (1974).

Maycumber, H. C., "Arsenic Residues in Cattle Grazed in Treated Areas," contained in: L. A. Norris (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

McBride, B. C., and R. S. Wolfe, "Biosynthesis of Dimethylarsine by Methanobacterium," *Biochemistry*, 10(23):4312-4317 (1971).

McCann, J. A., Chemical and Biological Investigation Branch, Office of Pesticide Programs, EPA, "Fish Toxicity Lab Report," EPA Pesticide Petition No. 9F0794 (1969).

Miller, C. W., and J. I. Lowe, "Toxicity of Herbicides to Estuarine Animals," U.S. Bureau of Commercial Fisheries Biological Laboratory, Gulf Breeze, Florida, unpublished report (1966).

Moffett, J. O., H. L. Morton, and R. H. Macdonald, "Toxicity of Some Herbicidal Sprays to Honey Bees," *J. Econ. Entomol.*, 65(1):32-36 (1972).

Morton, H. L., and J. O. Moffett, "Effects of Herbicides on Honey Bees," *Proc. West. Soc. Weed Sci.*, 25:15-16 (1972).

Morton, H. L., J. O. Moffett, and R. H. Macdonald, "Toxicity of Herbicides to Newly Emerged Honey Bees," *Environ. Entomol.*, 1(1):102-104 (1972).

Nagel, R. H., D. McComb, and F. B. Knight, "Trap Tree Method for Controlling the Engelmann Spruce Beetle in Colorado," *Journal of Forestry*, 55(12):894-898 (1957).

Newton, M., "Organic Arsenicals: Breakdown in Forest Trees and in Media Containing Energy Sources - A Progress Report," Oregon State University, Corvallis, Oregon, unpublished report submitted to the Environmental Protection Agency (1971).

Newton, M., and H. A. Holt, "Scolytid and Buprestid Mortality in Ponderosa Pines Injected with Organic Arsenicals," *J. Econ. Entomol.*, 64(4):952-958 (1971).

Norris, L. A., (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

Raab, H., *MSMA Museum Plots*, Ansul Test Station, Weslaco, Texas, The Ansul Company Report (1970).

Salman, H. A., T. R. Bartley, and A. D. Summers, *Progress Report of Residue Studies on Organic Arsenicals Used for Ditchbank Weed Control*, U.S. Department of the Interior, Bureau of Reclamation, Report REC-ERC-72-37, 8 pages (1972).

Sandberg, G. R., I. K. Allen, and E. A. Dietz, Jr., *Arsenic Residues in Soils Treated with Six Annual Applications of MSMA and Cacodylic Acid (CA)*, The Ansul Company, Marinette, Wisconsin, Report 73 Wes 8-9-10, Project No. 32532-73312, 82 p. (1973).

Sanders, H. O., "Toxicities of Some Herbicides to Six Species of Freshwater Crustaceans," *J. Water Pol. Cont. Fed.*, 42(8):1543-1550 (1970).

Schoettger, R. A., *Annual Progress Report, 1971*, U.S. Department of the Interior, Fish-Pesticide Laboratory, Fish and Wildlife Service, Columbia, Missouri (1971).

Schroedel, T., H. Hartwell, L. A. Norris, and J. Allard, "Arsenical Silvicide Effects on Wildlife," contained in: L. A. Norris (ed.), "The Behavior and Impact of Organic Arsenical Herbicides in the Forest Environment: An Interim Report on Cooperative Studies," unpublished report, Pacific Northwest Forest and Range Experiment Station, Corvallis, Oregon (1971).

Schweizer, E. E., *Effects of Residues of DSMA in Soils on Cotton, Soybeans, and Cereal Crops*, Mississippi State University, Agricultural Experiment Station, State College, Mississippi, Bulletin 736 (1967a).

Schweizer, E. E., "Toxicity of DSMA Soil Residues to Cotton and Rotational Crops," *Weeds*, 15(1):72-76 (1967b)

Stojanovic, B. J., M. V. Kennedy, and F. L. Shuman, Jr., "Edaphic Aspects of the Disposal of Unused Pesticides, Pesticide Wastes, and Pesticide Containers," *J. Environ. Qual.*, 1(1):54-62 (1972).

U. S. Department of the Interior, Fish and Wildlife Service, unpublished data from Fish-Pesticide Laboratory, Columbia, Missouri (1968).

Von Endt, D. W., P. C. Kearney, and D. D. Kaufman, "Degradation of Monosodium Methanearsonic Acid by Soil Microorganisms," Agr. Food Chem., 16(1):17-20 (1968).

Wiersma, G. B., H. Tai, and P. F. Sand, "Pesticide Residue Levels in Soils, FY 1969-National Soils Monitoring Program," Pest. Monit. J., 6(3):194-201 (1972).

Woolson, E. A., "Organoarsenical Herbicides," contained in: P. C. Kearney and D. D. Kaufman (eds.), Degradation of Herbicides, 2nd ed., Marcel Dekker, Inc., New York, New York, in press (1974).

Woolson, E. A., J. H. Axley, and P. C. Kearney, "Arsenic Research Summary," U.S. Department of Agriculture, Agricultural Research Service, Crops Protection Research Branch, Pesticide Investigations, unpublished report (1970a).

Woolson, E. A., P. C. Kearney, and J. H. Axley, "Chemical Distribution of Arsenic in Soils," U.S. Department of Agriculture, Agricultural Research Service, Crops Protection Research Branch, Pesticide Investigations, unpublished report (1970b).

Woolson, E. A., P. C. Kearney, A. R. Isensee, W. G. McShane, K. J. Irgolic, and R. A. Zingaro, "Bound Arsenic Fractions in a Crustacean," American Chemical Soc., Division of Pesticide Chemistry, 168th National Meeting, Atlantic City, New Jersey (1974).

Zabel, R. A., and F. W. O'Neil, "The Toxicity of Arsenical Compounds to Miccroorganisms," TAPPI, 40(11):911-914 (1957).

PART II. INITIAL SCIENTIFIC REVIEW

SUBPART D. PRODUCTION AND USE

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This section contains data on the registration and on the production and uses of MSMA and DSMA. The section summarizes rather than interprets data reviewed.

Registered Uses of MSMA and DSMA

Federally Registered Uses - MSMA is the monosodium salt, and DSMA the disodium salt of methylarsonic acid (MAA). These two closely related methanearsonate herbicides provide postemergence control of a number of hard-to-kill grass weeds, including Johnson grass, nutsedge, dallisgrass, crabgrass, and several other weeds. MSMA and DSMA are contact herbicides. They must contact green plant tissues to be effective. Their exact mode of action is not known.

DSMA was the first methanearsonate to be commercially developed and marketed for weed control in cotton. MSMA became available somewhat later, but has in the interim achieved far greater volume than DSMA, especially for use on cotton. MSMA is more effective than DSMA, providing the same degree of weed control at somewhat lower rates. On the other hand, DSMA is somewhat safer to young cotton and is, therefore, preferred by some cotton growers, especially for early season applications.

MSMA and DSMA are currently offered for sale in the United States by about 9 different suppliers, in a variety of formulations, and in several combinations with other herbicide active ingredients (see the subsection on Formulations, p. 92).

MSMA and DSMA are currently registered in the United States for use as directed applications*on cotton; for use under bearing or nonbearing citrus trees, including grapefruit, oranges, lemons, limes, and tangerines. DSMA is also registered for use as a topical application on cotton (ground equipment or aerial application). MSMA is registered for use as a directed application in non-bearing deciduous fruit and nut orchards. MSMA and DSMA are also registered for weed control on drainage ditchbanks; for control of grass weeds and certain other weeds in lawn and ornamental turf; and for use on noncropland for the control of hard-to-kill grass weeds and certain other hardy weeds such as cocklebur, sandbur, ragweed, puncturevine, and tules in or along rights-of-way, fence rows, storage yards, and similar noncrop areas.[1]

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* Directed application means that the spray solution is not permitted to contact leaves, stems, or bark of the crop in which weeds are to be controlled.

[1] U.S. Environmental Protection Agency, *EPA Summary of Registed Pesticides*, Vol. I, p. D-82, M-27.

Tolerances established for MAA are recorded in the Code of Federal Regulations, Title 40, Part 180.289. They apply to both MSMA and DSMA. The only residue tolerances for MSMA and DSMA currently in effect are 0.35 ppm in or on citrus fruits, 0.7 ppm in or on cottonseed, and 0.9 ppm in cottonseed hulls. Tolerances for MSMA and DSMA residues in or on grapes and sugarcane are currently pending.

On cotton, MSMA may be used as a preplant and/or postemergence application, at the rate of 2.0 lb AI/acre. Preplant broadcast applications may be made if planting of cotton is delayed and weeds have already emerged. Cotton may be planted immediately following MSMA application. Applications after cotton emergence must be directed so as to keep the spray off cotton foliage. If needed, a second or repeat application may be made about 1 to 3 weeks after the first application. Only 1 directed spray should be applied if following a topical application of DSMA. MSMA and DSMA should only be applied when cotton is 3-4 in tall and before first bloom. The spray must be kept off cotton foliage.

DSMA is recommended on cotton only as a postemergence application, at the rate of 2.25 to 3.0 lb AI/acre. It can be applied postemergence as a directed or topical application. For topical treatments use 2.8 lb AI/acre at 40 to 50 gpa mixed with 1 or 2 quarts of a mild surfactant suitable for use on cotton either with ground or aerial equipment. Apply when cotton has 1-2 true leaves to first square and do not make topical applications after first square. One directed application of DSMA may be made following a topical application to weeds under the conditions previously mentioned for MSMA.

For weed control in bearing or nonbearing citrus groves, and in nonbearing agricultural plantings such as deciduous fruit and nut orchards, MSMA is recommended as a directed application at the rate of 2.0 to 4.0 lb AI/acre. For bearing and nonbearing citrus orchards DSMA is recommended as a directed application at the rate of 3 to 6 lb AI/acre.

DSMA is not registered for use in nonbearing deciduous fruit or nut orchards.

For weed control on noncropland, MSMA is registered and recommended at 2.25 to 4.5 lb AI/acre, or 4.5 to 9.0 lb AI/100 gal. DSMA is recommended for use on noncropland at 4.7 to 5.5 lb AI/100 gal.

For use on lawn and ornamental turf grass, both MSMA and DSMA are recommended at the rate of 1.0 oz AI/1,000 ft^2 for smaller areas, or 2.7 to 6.0 lb AI/acre. MSMA and DSMA should be used only on established lawns and turf, and not at all on lawns consisting of Saint Augustine, bahiagrass, or centipede grass, or on dichondra lawns.

For an overview of these registrations, including the range of dosage rates, general and specific directions for use, use limitations, caution statements, and other details pertinent to commercial use, specimen labels for a typical, widely used MSMA liquid formulation (Ansar 529 H.C. containing 47.74% MSMA, equivalent to 6.0 lb MSMA/gal, by The Ansul Company, EPA Registration No. 6308-29) and for DSMA powder (containing 63.0% DSMA Anhydrous, equivalent to 100% DSMA hexahydrate, by the Diamond Shamrock Corporation, Agricultural Chemicals Division, EPA Registration No. 677-203-AA) are included in this section (Tables 5 and 6).

The MSMA 6 lb/gal label (Table 5) includes directions for use on cotton, bearing and nonbearing citrus, agricultural plantings, noncropland, and lawn and ornamental turf. The DSMA powder label (Table 6) includes directions for use on cotton, ornamental turf grass, and noncropland.

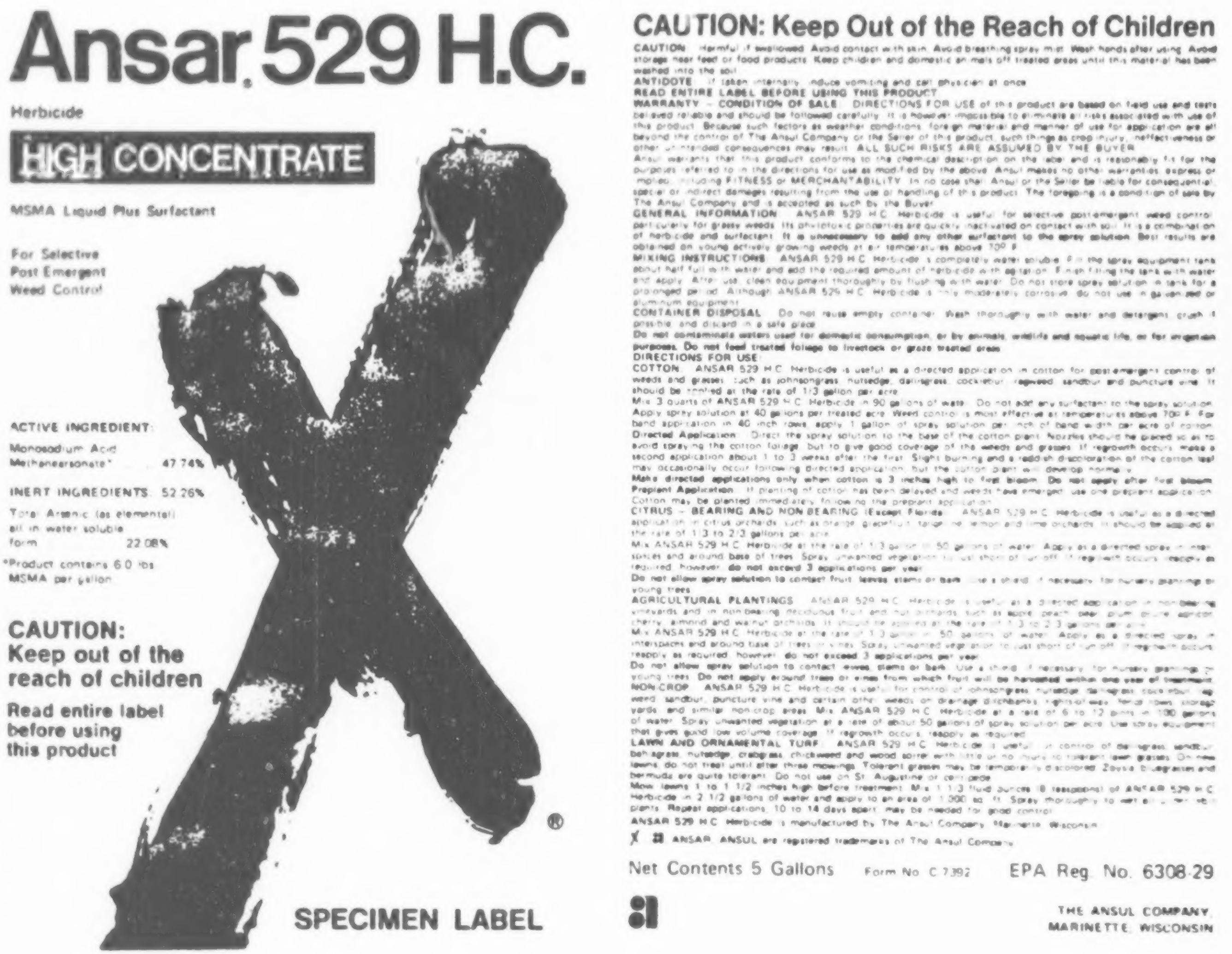
Table 7 presents an activity profile for MSMA on about 120 different weed species. Among these, Johnson grass (*Sorghum halepense*), nutsedge (*Cyperus* sp.), dallisgrass (*Paspalum dilatatum*), cocklebur (*Xanthium* sp.), ragweed (*Ambrosia* sp.), sandbur (*Cenchrus* sp.), and puncturevine (*Tribulus terrestris*) are economically most important regarding the use of MSMA and DSMA in the United States.

State Regulations - Toxicity studies indicate that MSMA and DSMA are not highly toxic to mammals (see the subsection on Pharmacology and Toxicology, p. 37). The two herbicides are rated "slightly toxic" with regard to mammalian toxicity. Some states that regulate the use of pesticides have placed special restrictions on pesticides which are highly toxic or otherwise hazardous to man and/or environmental health. For instance, in California, 42 pesticides have been designated as "injurious or restricted materials." The use of pesticides in this category is subject to special restrictions under regulations administered by the State Department of Agriculture. The California list of "injurious materials" includes "certain arsenic compounds," including inorganic trivalent arsenicals and inorganic pentavalent arsenates, but not organic pentavalent arsenicals including MSMA and DSMA. Thus, these herbicides are neither subject to special regulations in California nor, as far as is known, in any other state.

In the Federally registered labels of MSMA products, directions for use on cotton do not include provisions for aerial applications, nor do they specifically recommend against application by aircraft. Several cotton growing states, including Arkansas, Louisiana, and Mississippi, permit the application of MSMA by aircraft prior to planting, or up to the "cracking" stage of cotton. Aircraft applications may be made to prepared seedbeds when planting of cotton has been delayed and weeds have emerged, or as a postplant treatment, but no later than initial cracking of soil in the field before emergence of cotton, or a maximum of 5 days after planting, whichever occurs first.

Aircraft applications may be made only during these periods, but must not be made after emergence of the cotton. The Cooperative Extension Service recommendations for cotton weed control in Arkansas, Louisiana and Mississippi do not recommend such aerial applications, but suppliers of MSMA formulations provide special directions for application by aircraft to users in the states mentioned.

Table 5. MSMA 6 LB/GAL (47.74%) LIQUID CONCENTRATE SPECIMEN LABEL



Ansar® 529 H.C.

Herbicide

HIGH CONCENTRATE

MSMA Liquid Plus Surfactant

For Selective
Post Emergent
Weed Control

ACTIVE INGREDIENT:

Monosodium Acid Methanearsonate*	47.74%
INERT INGREDIENTS:	52.26%
Total Arsenic (as elemental) all in water soluble form	22.08%

*Product contains 6.0 lbs MSMA per gallon

CAUTION:
Keep out of the reach of children

Read entire label before using this product

SPECIMEN LABEL

CAUTION: Keep Out of the Reach of Children

CAUTION: Harmful if swallowed. Avoid contact with skin. Avoid breathing spray mist. Wash hands after using. Avoid storage near feed or food products. Keep children and domestic animals off treated areas until this material has been washed into the soil.

ANTIDOTE: If taken internally, induce vomiting and call physician at once.

READ ENTIRE LABEL BEFORE USING THIS PRODUCT

WARRANTY – CONDITION OF SALE: DIRECTIONS FOR USE of this product are based on field use and tests believed reliable and should be followed carefully. It is however impossible to eliminate all risks associated with use of this product. Because such factors as weather conditions, foreign material and manner of use for application are all beyond the control of The Ansul Company or the Seller of this product, such things as crop injury, ineffectiveness or other unintended consequences may result. ALL SUCH RISKS ARE ASSUMED BY THE BUYER.

Ansul warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes referred to in the directions for use as modified by the above. Ansul makes no other warranties, express or implied, including FITNESS or MERCHANTABILITY. In no case shall Ansul or the Seller be liable for consequential, special or indirect damages resulting from the use or handling of this product. The foregoing is a condition of sale by The Ansul Company and is accepted as such by the Buyer.

GENERAL INFORMATION: ANSAR 529 H.C. Herbicide is useful for selective post-emergent weed control, particularly for grassy weeds. Its phytotoxic properties are quickly inactivated on contact with soil. It is a combination of herbicide and surfactant. **It is unnecessary to add any other surfactant to the spray solution.** Best results are obtained on young actively growing weeds at air temperatures above 70° F.

MIXING INSTRUCTIONS: ANSAR 529 H.C. Herbicide is completely water soluble. Fill the spray equipment tank about half full with water and add the required amount of herbicide with agitation. Finish filling the tank with water and apply. After use, clean equipment thoroughly by flushing with water. Do not store spray solution in tank for a prolonged period. Although ANSAR 529 H.C. Herbicide is only moderately corrosive, do not use in galvanized or aluminum equipment.

CONTAINER DISPOSAL: Do not reuse empty container. Wash thoroughly with water and detergent, crush if possible, and discard in a safe place.

Do not contaminate waters used for domestic consumption, or by animals, wildlife and aquatic life, or for irrigation purposes. Do not feed treated foliage to livestock or graze treated areas.

DIRECTIONS FOR USE:

COTTON: ANSAR 529 H.C. Herbicide is useful as a directed application in cotton for post-emergent control of weeds and grasses such as johnsongrass, nutsedge, dallisgrass, cocklebur, ragweed, sandbur and puncture vine. It should be applied at the rate of 1/3 gallon per acre.

Mix 3 quarts of ANSAR 529 H.C. Herbicide in 90 gallons of water. Do not add any surfactant to the spray solution. Apply spray solution at 40 gallons per treated acre. Weed control is most effective at temperatures above 70° F. For band application in 40 inch rows, apply 1 gallon of spray solution per inch of band width per acre of cotton.

Directed Application: Direct the spray solution to the base of the cotton plant. Nozzles should be placed so as to avoid spraying the cotton foliage, but to give good coverage of the weeds and grasses. If regrowth occurs, make a second application about 1 to 3 weeks after the first. Slight burning and a reddish discoloration of the cotton leaf may occasionally occur following directed application, but the cotton plant will develop normally.

Make directed applications only when cotton is 3 inches high to first bloom. Do not apply after first bloom.

Preplant Application: If planting of cotton has been delayed and weeds have emerged, use one preplant application. Cotton may be planted immediately following the preplant application.

CITRUS – BEARING AND NON-BEARING (Except Florida): ANSAR 529 H.C. Herbicide is useful as a directed application in citrus orchards such as orange, grapefruit, tangerine, lemon and lime orchards. It should be applied at the rate of 1/3 to 2/3 gallons per acre.

Mix ANSAR 529 H.C. Herbicide at the rate of 1/3 gallon in 50 gallons of water. Apply as a directed spray in interspaces and around base of trees. Spray unwanted vegetation to just short of run off. If regrowth occurs, reapply as required; however, **do not exceed 3 applications per year.**

Do not allow spray solution to contact fruit, leaves, stems or bark. Use a shield, if necessary, for nursery plantings or young trees.

AGRICULTURAL PLANTINGS: ANSAR 529 H.C. Herbicide is useful as a directed application in non-bearing vineyards and in non-bearing deciduous fruit and nut orchards such as apple, peach, pear, plum, prune, apricot, cherry, almond and walnut orchards. It should be applied at the rate of 1/3 to 2/3 gallons per acre.

Mix ANSAR 529 H.C. Herbicide at the rate of 1/3 gallon in 50 gallons of water. Apply as a directed spray in interspaces and around base of trees or vines. Spray unwanted vegetation to just short of run off. If regrowth occurs, reapply as required; however, **do not exceed 3 applications per year.**

Do not allow spray solution to contact leaves, stems or bark. Use a shield, if necessary, for nursery plantings or young trees. **Do not apply around trees or vines from which fruit will be harvested within one year of treatment.**

NON-CROP: ANSAR 529 H.C. Herbicide is useful for control of johnsongrass, nutsedge, dallisgrass, cocklebur, ragweed, sandbur, puncture vine and certain other weeds on drainage ditchbanks, rights-of-way, fence rows, storage yards, and similar non-crop areas. Mix ANSAR 529 H.C. Herbicide at a rate of 6 to 12 pints in 100 gallons of water. Spray unwanted vegetation at a rate of about 50 gallons of spray solution per acre. Use spray equipment that gives good low volume coverage. If regrowth occurs, reapply as required.

LAWN AND ORNAMENTAL TURF: ANSAR 529 H.C. Herbicide is useful in control of dallisgrass, sandbur, bahiagrass, nutsedge, crabgrass, chickweed and wood sorrel with little or no injury to tolerant lawn grasses. On new lawns, do not treat until after three mowings. Tolerant grasses may be temporarily discolored. Zoysia, bluegrasses and bermuda are quite tolerant. Do not use on St. Augustine or centipede.

Mow lawns 1 to 1 1/2 inches high before treatment. Mix 1 1/3 fluid ounces (8 teaspoons) of ANSAR 529 H.C. Herbicide in 2 1/2 gallons of water and apply to an area of 1,000 sq. ft. Spray thoroughly to wet all unwanted plants. Repeat applications, 10 to 14 days apart, may be needed for good control.

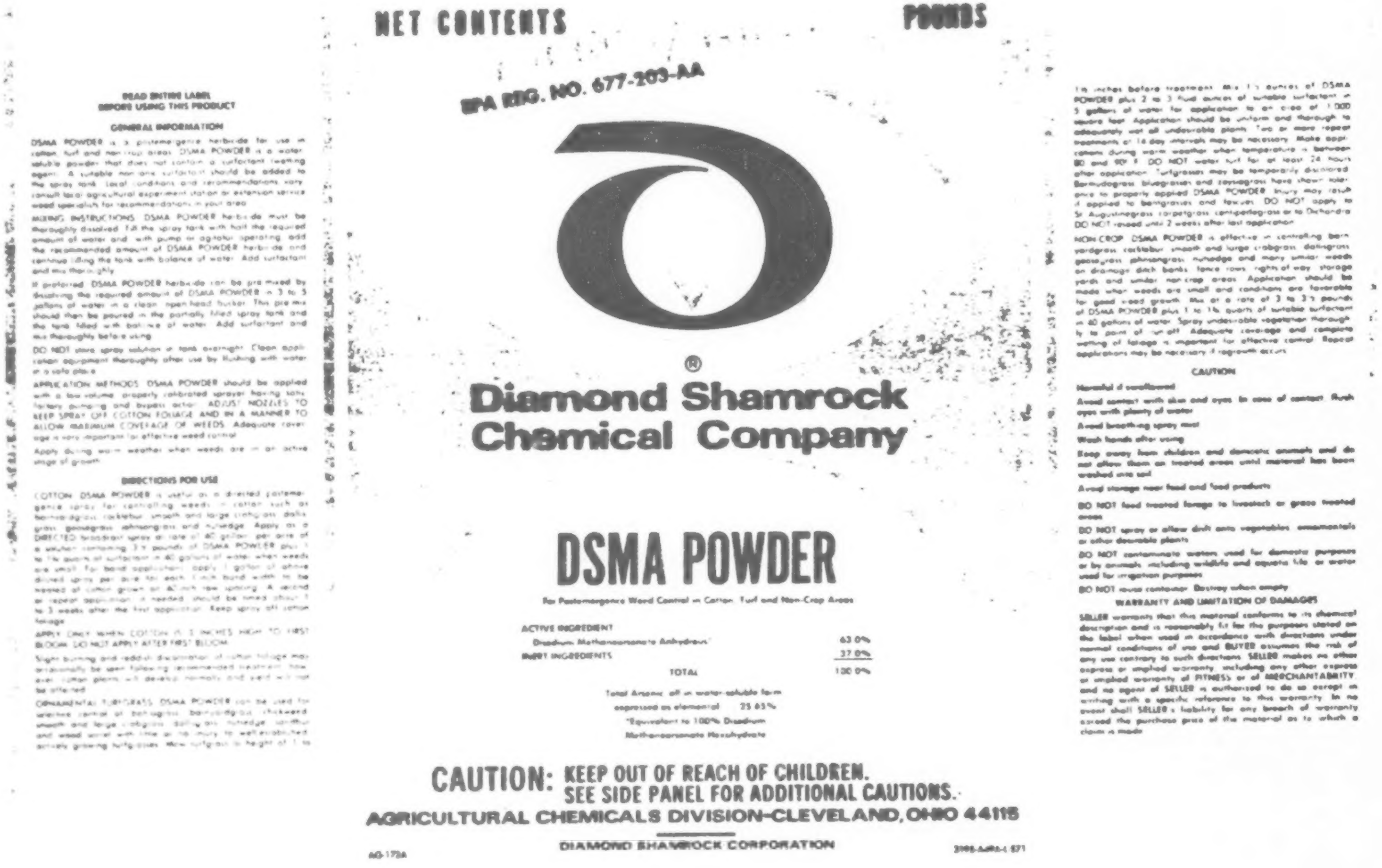
ANSAR 529 H.C. Herbicide is manufactured by The Ansul Company, Marinette, Wisconsin.

X, ANSAR, ANSUL are registered trademarks of The Ansul Company.

Net Contents 5 Gallons Form No. C 7392 EPA Reg. No. 6308-29

THE ANSUL COMPANY,
MARINETTE, WISCONSIN

Table 6. DSMA SOLUBLE POWDER (63%) SPECIMEN LABEL



READ ENTIRE LABEL
BEFORE USING THIS PRODUCT

GENERAL INFORMATION

DSMA POWDER is a postemergence herbicide for use in cotton, turf and non-crop areas. DSMA POWDER is a water-soluble powder that does not contain a surfactant (wetting agent). A suitable non-ionic surfactant should be added to the spray tank. Local conditions and recommendations vary; consult local agricultural experiment station or extension service weed specialists for recommendations in your area.

MIXING INSTRUCTIONS: DSMA POWDER herbicide must be thoroughly dissolved. Fill the spray tank with half the required amount of water and, with pump or agitator operating, add the recommended amount of DSMA POWDER herbicide and continue filling the tank with balance of water. Add surfactant and mix thoroughly.

If preferred, DSMA POWDER herbicide can be pre-mixed by dissolving the required amount of DSMA POWDER in 3 to 5 gallons of water in a clean, open-head bucket. This pre-mix should then be poured in the partially filled spray tank and the tank filled with balance of water. Add surfactant and mix thoroughly before using.

DO NOT store spray solution in tank overnight. Clean application equipment thoroughly after use by flushing with water in a safe place.

APPLICATION METHODS: DSMA POWDER should be applied with a low-volume, properly calibrated sprayer having satisfactory pumping and bypass action. ADJUST NOZZLES TO KEEP SPRAY OFF COTTON FOLIAGE AND IN A MANNER TO ALLOW MAXIMUM COVERAGE OF WEEDS. Adequate coverage is very important for effective weed control.

Apply during warm weather when weeds are in an active stage of growth.

DIRECTIONS FOR USE

COTTON: DSMA POWDER is useful as a directed postemergence spray for controlling weeds in cotton such as barnyardgrass, cocklebur, smooth and large crabgrass, dallisgrass, goosegrass, johnsongrass and nutsedge. Apply as a DIRECTED broadcast spray at rate of 40 gallons per acre of a solution containing 3½ pounds of DSMA POWDER plus 1 to 1½ quarts of surfactant in 40 gallons of water when weeds are small. For band applications, apply 1 gallon of above diluted spray per acre for each 1 inch band width to be treated of cotton grown on 40-inch row spacing. A second or repeat application, if needed, should be timed about 1 to 3 weeks after the first application. Keep spray off cotton foliage.

APPLY ONLY WHEN COTTON IS 3 INCHES HIGH TO FIRST BLOOM. DO NOT APPLY AFTER FIRST BLOOM.

Slight burning and reddish discoloration of cotton foliage may occasionally be seen following recommended treatment; however, cotton plants will develop normally and yield will not be affected.

ORNAMENTAL TURFGRASS: DSMA POWDER can be used for selective control of bahiagrass, barnyardgrass, chickweed, smooth and large crabgrass, dallisgrass, nutsedge, sandbur and wood sorrel with little or no injury to well-established, actively growing turfgrasses. Mow turfgrass to height of 1 to 1½ inches before treatment. Mix 1½ ounces of DSMA POWDER plus 2 to 3 fluid ounces of suitable surfactant in 5 gallons of water for application to an area of 1,000 square feet. Application should be uniform and thorough to adequately wet all undesirable plants. Two or more repeat treatments at 14-day intervals may be necessary. Make applications during warm weather when temperature is between 80 and 90° F. DO NOT water turf for at least 24 hours after application. Turfgrasses may be temporarily discolored. Bermudagrass, bluegrasses and zoysiagrass have shown tolerance to properly applied DSMA POWDER. Injury may result if applied to bentgrasses and fescues. DO NOT apply to St. Augustinegrass, carpetgrass, centipedegrass or to Dichondra. DO NOT reseed until 2 weeks after last application.

NON-CROP: DSMA POWDER is effective in controlling barnyardgrass, cocklebur, smooth and large crabgrass, dallisgrass, goosegrass, johnsongrass, nutsedge and many similar weeds on drainage ditch banks, fence rows, rights-of-way, storage yards and similar non-crop areas. Application should be made when weeds are small and conditions are favorable for good weed growth. Mix at a rate of 3 to 3½ pounds of DSMA POWDER plus 1 to 1½ quarts of suitable surfactant in 40 gallons of water. Spray undesirable vegetation thoroughly to point of run-off. Adequate coverage and complete wetting of foliage is important for effective control. Repeat applications may be necessary if regrowth occurs.

CAUTION

Harmful if swallowed.

Avoid contact with skin and eyes. In case of contact, flush eyes with plenty of water.

Avoid breathing spray mist.

Wash hands after using.

Keep away from children and domestic animals and do not allow them on treated areas until material has been washed into soil.

Avoid storage near food and food products.

DO NOT feed treated forage to livestock or graze treated areas.

DO NOT spray or allow drift onto vegetables, ornamentals or other desirable plants.

DO NOT contaminate waters used for domestic purposes or by animals, including wildlife and aquatic life, or water used for irrigation purposes.

DO NOT reuse container. Destroy when empty.

WARRANTY AND LIMITATION OF DAMAGES

SELLER warrants that this material conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions under normal conditions of use and BUYER assumes the risk of any use contrary to such directions. SELLER makes no other express or implied warranty, including any other express or implied warranty of FITNESS or of MERCHANTABILITY, and no agent of SELLER is authorized to do so except in writing with a specific reference to this warranty. In no event shall SELLER's liability for any breach of warranty exceed the purchase price of the material as to which a claim is made.

NET CONTENTS **POUNDS**

EPA REG. NO. 677-203-AA

Diamond Shamrock®
Chemical Company

DSMA POWDER

For Postemergence Weed Control in Cotton, Turf and Non-Crop Areas

ACTIVE INGREDIENT	
Disodium Methanearsonate Anhydrous*	63.0%
INERT INGREDIENTS	37.0%
TOTAL	100.0%

Total Arsenic, all in water-soluble form
expressed as elemental 25.65%
*Equivalent to 100% Disodium
Methanearsonate Hexahydrate

CAUTION: KEEP OUT OF REACH OF CHILDREN.
SEE SIDE PANEL FOR ADDITIONAL CAUTIONS.

AGRICULTURAL CHEMICALS DIVISION–CLEVELAND, OHIO 44115

DIAMOND SHAMROCK CORPORATION

AG-173A [illegible]

Table 7. WEED CONTROL PROFILE OF MSMA

COMMON NAME		LATIN NAME	DEGREE OF CONTROL WITH MSMA*		
			2-3 lbs	4-6 lbs	7-9 lbs
Ageratum, tropic		Ageratum conyzoides	very good		
Amaranth, spiny	a	Amaranthus spinosus			
Angeltongrass	p	Andropogon annulatus	good		
Aster, whiteheath	p	Aster pilosus			
Bamboo grass		Ischaemum mutican/I. timorense	very good		
Barley, little	a	Hordeum pusillum	tolerant		
Barnyardgrass	a	Echinochloa crusgalli	fair		
Beggarweed, Florida	a	Desmodium tortuosum			
Bermudagrass	p	Cynodon dactylon	tolerant		
Betony, Florida	p	Stachys floridana			
Bindweed, field	p	Convolvulus arvensis	stunting	good at first bloom	
Bitterweed	a	Helenium tenuifolium			
Blackberry	b	Rubus sp			
Blackseedgrass		Sprorbolus indicus	fair to good		
Bluegrass, annual	a	Poa annua	tolerant		
Bluegrass, Kentucky	p	Poa pratensis	tolerant		
Bracken, Eastern	a	Pteridium aquilinum			
Brome, downy	a	Bromus tectorum	fair late spring		
Bromegrass		Bromus sp	tolerant		
Broomsedge	p	Andropogon virginicus			
Buckwheat, wild	a	Polygonum convolvulus	fair		
Buffelgrass		Pennisetum ciliare	good		
Bulrush	p	Scirpus sp	good		
Burcucumber	a	Sicyos angulatus			
Bursage, woolyleaf		Franseria tomentosa			
Buttercup	a	Ranunculus sp.			
Camphorweed	a or b	Heterotheca subaxillaris			
Canarygrass, Reed		Phalaris arundinacea	tolerant	tolerant	tolerant
Careless weed	a	Amaranthus palmeri	good		
Carpetgrass		Axonopus affinis	excellent		
Carpetweed	a	Mollugo verticillata			
Carrot, wild	b	Daucus carota	tolerant		
Cheatgrass		Bromus secalinus		excellent late spring	
Chickweed	a	Stellaria media			
Chickweed, field	p	Cerastium arvense	good		
Chickweed, mouseear	p	Cerastium vulgatum	good		
Chickweed, sticky		Cerastium visconsum	good		
Chompipe		Ixuphorus unisetus	excellent		
Cocklebur, common	a	Xanthium pennsylvanicum	good		
Cockle, corn	a	Agrostemma githago			
Coffeeweed	a	Sesbania sp	tolerant		
Cogongrass		Imperata cylindrica	tolerant		
Copperleaf, Virginia	a	Acalypha virginica			
Cornflower	a	Centaurea cyanus			
Crabgrass, hairy	a	Digitaria sanguinalis	good		
Crabgrass, large	a	Digitaria sanguinalis	good		
Crabgrass, small	a	Digitaria ischaemum	good		
Crabgrass, smooth	a	Digitaria ischaemum	good		
Cress, hoary	p	Cardaria draba			
Crotalaria, showy	a	Crotalaria spectabilis			
Croton, tropic	a	Croton glandulosus			
Croton, wooly	a	Croton capitatus			
Crowfootgrass	a	Dactyloctenium aegyptium			
Cucumber, wild	a	Echinocystis lobata			
Cudweed	b	Gnaphalium sp.			
Dallisgrass	p	Paspalum dilatatum	good		
Dandelion	p	Taraxacum officinale	tolerant		
Dayflower	a	Commelina communis			
Dichondra	p	Dichondra repens			
Dock, broadleaf	p	Rumex obtusifolius			
Dock, curly	p	Rumex crispus			
Dodder, field	a	Cuscuta campestris			
Dogbane, hemp	p	Apocynum cannabinum			
Dogfennel	p	Eupatorium capillifolium			
Dropseed, Indian		Sporobolus diander	fair to good		
Drymary, heartleaf	a	Drymaria cordata			

Source: The Ansul Company, "Weeds Controlled by MSMA," Marinette, Wisconsin (1972).

Table 7. (Continued)

COMMON NAME	LATIN NAME		DEGREE OF CONTROL WITH MSMA*		
			2 3 lbs	4 6 lbs	7 9 lbs
Eveningprimrose, cutleaf	a	Oenothera laciniata			
Falsedandelion, Carolina	a or b	Pyrrhopappus carolinianus			
Fescue, tall		Festuca sp	tolerant		
Fiddleneck		Amsinckia douglasiana	fair	good	
Filaree, redstem	a or b	Erodium cicutarium	fair in spring		
Fingergrass, swollen		Chloris inflata	good		
Flax, common		Linum usitatissimum			
Fleabane, annual	a or b	Erigeron annuus			
Fleabane, daisy	a	Erigeron strigosus			
Flixweed	a	Descurainia sophia			
Foxtail, giant	a	Setaria faberii	good		
Foxtail, green	a	Setaria viridis	good		
Foxtail, yellow	a	Setaria glauca	good		
Galinsoga, hairy	a	Galinsoga ciliata			
Garlic, wild	p	Allium vineale			
Geranium, Carolina	a or b	Geranium carolinianum			
German weed		Borreria latifolia	good		
Goldenrod	p	Solidago sp			
Goosegrass	a	Eleusine indica	fair		
Greenbrier, common	p	Smilax rotundifolia			
Gromwell		Lithospermum officinale		excellent	
Groundcherry, clammy	p	Physalis heterophylla			
Groundcherry, longleaf	p	Physalis longifolia	very good on young plants		
Groundcherry, smooth	p	Physalis subglabrata			
Groundsel	p	Senecio sp			
Hempweed, climbing		Mikania scandens	good		
Henbit	a	Lamium amplexicaule	good		
Hilograss		Paspalum conjugatum	excellent		
Honeysuckle, Japanese	p	Lonicera japonica			
Horsenettle	p	Solanum carolinense			
Horseweed	a	Erigeron canadensis			
Jimsonweed	a	Datura stramonium	tolerant		
Johnsongrass	p	Sorghum halepense	good		
Kikuyu grass		Pennisetum clandestinum	good		
Knapweed, Russian	p	Centaurea repens			
Knotweed	a	Polygonum sp			
Kochia		Kochia scoparia			
Kudzu	p	Pueraria lobata			
Lalang		Imperata cylindrica	tolerant		
Lambsquarter, common	a	Chenopodium album	good	excellent	
Lettuce, miners		Montia perfoliata			
Lettuce, wild	a	Lactuca scariola			
Lovegrass, feather	a	Eragrostis amabilis	fair to good		
Mallow, purple poppy		Callirhoe involucrata	good		
Mayweed	a	Anthemis cotula			
Medusa head	a	Taeniatherum asperum			
Melastoma, Banks		Melastoma malabathricum	fair		
Milkweed, butterfly	p	Asclepias tuberosa			
Milkweed, honeyvine	p	Ampelamus albidus			
Morningglory, annual	a	Ipomoea purpurea	good		
Morningglory, bigroot	p	Ipomoea pandurata			
Morningglory, cypressvine	a	Ipomoea quamoclit			
Morningglory, ivyleaf	a	Ipomoea hederacea	good		
Morningglory, smallflower	a	Jaquemontia tamnifolia			
Morningglory, tall	a	Ipomoea purpurea	good		
Morningglory, wild	p	Convolvulus arvensis	good	excellent at full bloom	
Mullein, common	b	Verbascum thapsus			
Mullein, Turkey		Eremocarpus setigerus			
Mustard, blue		Chorispora tenella		excellent	
Mustard, tansy	a	Descurainia pinnata	fair to good		
Mustard, tumble		Sisymbrium altissimum		good	
Mustard, wild	a	Brassica kaber	good		
Nightshade, black	a	Solanum nigrum			
Nightshade, silverleaf	p	Solanum elaeagnifolium		good	

Table 7. (Continued)

COMMON NAME		LATIN NAME	DEGREE OF CONTROL WITH MSMA* 2 3 lbs	4 6 lbs	7 9 lbs
Nimblewill	p	Muhlenbergia schreberi			
Nutsedge, purple	p	Cyperus rotundus	good		
Nutsedge, yellow	p	Cyperus esculentus	good		
Oats, wild	a	Avena fatua	good to excellent		
Onion, wild	p	Allium canadense			
Orchardgrass	p	Dactylis glomerata	tolerant		
Panicum, fall	a	Panicum dichotomiflorum	good		
Panicum, Texas	a	Panicum texanum			
Partridge pea	a	Cassia fasciculata			
Paspalum, Panama		Paspalum fimbriatum	good		
Paspalum, sour		Paspalum conjugatum	excellent		
Passionflower, maypop	p	Passiflora incarnata			
Passionflower, redfruit		Passiflora foetida	very good		
Peppervine	p	Ampelopsis arborea			
Pepperweed, Virginia	a or b	Lepidium virginicum			
Pigweed, redroot		Amaranthus retroflexus			
Pigweed, rough	a	Amaranthus retroflexus	good		
Plantain, bracted	a	Plantago aristata			
Plantain, broadleaf	p	Plantago major			
Plantain, buckhorn	p	Plantago lanceolata			
Poison ivy	p	Rhus radicans			
Pokeberry	p	Phytolacca americana			
Poorjoe	a	Diodia teres			
Prickly pear	p	Opuntia sp.			
Puncturevine	a	Tribulus terrestris	good		
Purslane, common	a	Portulaca oleracea	fair		
Purslane, Florida	a	Richardia scabra			
Pusley	a	Richardia scabra			
Quackgrass	p	Agropyron repens	tolerant		
Ragweed, common	a	Ambrosia artemisiifolia	good		
Ragweed, giant	a	Ambrosia trifida	good		
Raoulgrass		Rottboellia exaltata	excellent		
Rattlebox		Crotalaria sagittalis	fair		
Redtop		Agrostis alba	tolerant		
Redvine	p	Brunnichia cirrhosa			
Rhodesgrass		Chloris gayana	tolerant		
Rice, jungle	a	Echinochloa colonum	fair		
Rocket, London		Sisymbrium irio	good		
St. Augustinegrass	p	Stenotaphrum secundatum	good		
Saltbush, Wright		Atriplex wrightii		good to excellent	
Saltgrass, desert		Distichlis stricta		good early	
Sandbur, field	a	Cenchrus pauciflorus	good		
Sandbur, Southern	a	Cenchrus echinatus	good		
Sedge, giant		Hypolytrum latifolium	good		
Sedgegrass		Scleria sumatrensis	very good		
Sensitiveplant		Mimosa pudica	fair to good		
Sensitiveplant, giant		Mimosa invisa	good		
Sesbania, hemp	a	Sesbania exaltata			
Shepherdspurse	a	Capsella bursa-pastoris			
Siam weed	p	Eupatorium odoratum	fair to good		
Sicklepod	a	Cassia tora			
Sicklepod	a	Cassia obtusifolia			
Sida, prickly	a	Sida spinosa			
Signalgrass, broadleaf	a	Brachiaria platyphylla	good		
Smartweed, Pennsylvania	a	Polygonum pennsylvanicum	poor		
Smutgrass	p	Sporobolus poiretii	fair to good		
Sneezeweed, bitter	a	Helenium amarum			
Sorrel, red	p	Rumex acetosella			
Sowthistle, spiny	a	Sonchus asper	tolerant		
Spanish needles	a	Bidens bipinnata			
Sprangletop	a	Leptochloa imbricata			
Sprangletop, red	a	Leptochloa filiformis	tolerant		
Spurge, spotted	a	Euphorbia maculata		excellent	
Starbur, bristly	a	Acanthospermum hispidum			
Stargrass, Australian		Chloris divaricata	good		

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Table 7. (Continued)

			DEGREE OF CONTROL WITH MSMA*		
COMMON NAME	LATIN NAME		2-3 lbs	4-6 lbs	7-9 lbs.
Stinkgrass	a	Eragrostis cilianensis	poor		
Stork's bill	a or b	Erodium cicutarium	fair in spring		
Sunflower	a	Helianthus annuus	good		
Swinecress	a or b	Coronopus didymus			
Thistle, blessed	a	Cnicus benedictus			
Thistle, Canada	p	Cirsium arvense			
Thistle, Russian	a	Salsola Kali	fair in spring on young plants	good early	
Thistle, yellow star		Centaurea solstitialis			
Timothy		Phleum pratense	poor		
Torpedograss	p	Panicum repens			
Trumpetcreeper	p	Campsis radicans			
Tules	p	Scirpus sp.	good		
Vaseygrass	p	Paspalum urvillei			
Velvetleaf	a	Abutilon theophrasti	tolerant		
Verbena, roadside	a	Verbena hastata			
Vervain, blue	a	Verbena hastata			
Vervain, prostrate	a	Verbena rigida			
Vetch, narrowleaf	a	Vicia angustifolia	good		
Wallflower, Western		Erysimum asperum			
Watergrass	a	Echinochloa crysgalli	good		
Watermelon, wild	a	Citrullus vulgaris			
Wheatgrass, crested	p	Agropyron cristatum			
Wildergrass	p	Andropogon nodosus	good		
Witchgrass	a	Panicum capillare	good		
Witchweed	a	Striga lutea			
Woodsorrel, common yellow	a	Oxalis stricta			
Woodsorrel, creeping		Oxalis corniculata	good		
Yarrow, common	p	Achillea millefolium			
Yerba de tugo	a	Eclipta alba			
		Asystasia coromandeliana	poor		
		Axonopus compressus	good		
		Bulbostylis sp	good		
		Centrosema pubescens	poor		
		Cyclosorus gonyloides	good		
		Cyrtococcum accrescens	good		
		Eragrostis elongata	tolerant		
		Lygodium flexuosum	good to very good		
		Lygodium scandens	good to very good		
		Panicum nodosum	fair		
		Panicum pilipes	good		
		Paspalum commersonii	excellent		
		Paspalum scrobiculatum	excellent		
		Pityrogramma calomelanai	good to very good		
		Stenochlaena palustris	fair to good		

*Degree of Control

Tolerant	0	10% Control
Poor	10	60% Control
Fair	60	75% Control
Good	75	95% Control
Excellent	95	100% Control

a = annual plant
b = biennial plant
p = perennial plant

In regard to DSMA, at least one formulation has received Federal approval for aerial application as of July 16, 1975 (Ansar 8100 herbicide-high concentrate DSMA powder, 81.0% disodium methanearsonate). For aerial applications of DSMA formulations, special attention should be given to recommended rates and timing of application (as related to the growth stage of the cotton), as well as prevailing weather conditions both prior to and at the time of application.

Production and Domestic Supply

Volume of Production - According to the United States Tariff Commission annual reports (1971, 1972, 1973),[1] there were four basic producers of methylarsonic acid salts as herbicides in the United States during the 1972-1973 period. MSMA was produced in each of the 3 years by 2 manufacturers -- the Ansul Company, Marinette, Wisconsin; and Diamond Shamrock Corporation, Cleveland, Ohio. DSMA was produced by 4 different companies in 1971 and 1972 -- Ansul; Diamond; the W. A. Cleary Corporation, New Brunswick, New Jersey; and Vineland Chemical Company, Vineland, New Jersey. In 1973, 3 companies, Ansul, Cleary and Vineland, produced DSMA. In addition to MSMA and DSMA, the category "methylarsonic acid salts" in the Tariff Commission reports includes the dodecyl- and octylammonium salts.

The Tariff Commission reported the following production volumes for MAA salts for the 1970-1973 period: 1970, 30,454,000 lb; 1971, 24,476,000 lb; 1972, 30,698,000 lb; 1973, 40,126,000 lb.

Thus, the total quantity of MAA herbicides produced in the United States varied from about 24 million lb in 1971 to 40 million lb in 1973.

MSMA was one of 25 selected pesticides whose production, distribution, use, and environmental impact potential were recently studied by Midwest Research Institute and RvR Consultants in a project funded jointly by the Council on Environmental Quality and the Environmental Protection Agency (von Rümker et al. 1974).[2] The base year for production and use estimates for that study was 1972. The U.S. production volume of MSMA in 1972 was estimated at 24 million lb AI. Of the remaining 6.7 million lb of other methanearsonate (30.7 million lb total less 24 million lb MSMA), about 6 million lb were estimated to be the DSMA; the balance was octyl- and dodecylammonium salts.

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[1] U.S. Tariff Commission, Synthetic Organic Chemicals, U.S. Production and Sales, TC Publication 681 (1971, 1972, 1973).

[2] von Rümker, R., E. W. Lawless, and A. F. Meiners, Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides, Final Report for Council on Environmental Quality, Washington, D.C., Contract No. EQC-311, 439 pp. (1974).

Imports - According to MRI, the absence of reported MAA imports from U.S. trade data indicates insignificant quantities imported.

Exports - The Bureau of Census (1972)[1] placed total exports of formulated herbicides at 38,867,237 lb, with no specific listing for MAA herbicides. However, MRI estimates 7 million lb AI of MSMA was exported.

Formulations - MSMA and DSMA are available to users in the United States in a number of different concentrates and formulations. Liquid concentrates are used most frequently. DSMA is also available in the form of dry soluble powders. MSMA is completely water soluble, and DSMA is highly soluble. Therefore, water is a very satisfactory solvent for liquid formulations of both materials, and more expensive organic solvents and emulsifiers are not required. However, surfactants are essential for good coverage of, and efficacy on, target weeds. Some liquid formulations contain varying amounts of surfactants, whereas others contain none. In the latter case, the user has to add his own surfactant to the spray tank. This is preferred by some users because it allows them to use a surfactant which works best with the local water, and to use just the amount of surfactant needed, based on previous experience.

MSMA and DSMA formulations are offered under a variety of different trade names or lines of trade names. Three companies offer herbicide products containing MSMA or DSMA in combination with other herbicides. These products include one containing MSMA plus sodium cacodylate; combinations of MSMA with fluometuron and prometryne, respectively; and one containing DSMA plus 2,4-D.

The most frequently used formulations are: 1) MSMA liquid concentrates containing 4, 6, or 8 lb AI/gal. These formulations are offered without or with varying amounts of surfactant(s) added. There are no significant dry powder or granular MSMA formulations on the market at present; 2) DSMA liquid concentrates and soluble powders containing from 20 to about 80% AI (DSMA used in anhydrous form, or as penta- or hexahydrate). Low-concentrate DSMA liquid or granular formulations (2 to 4% active ingredient) are offered for lawn weed control by amateur gardeners.

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[1] U.S. Bureau of the Census, U.S. Exports, Schedule B, Commodity by Country, Section 599.2080, Report FT 410 (1972).

About 40 different MSMA and DSMA herbicide products are listed in the Pesticide Handbook (Billings 1974).[1] The most popular formulations are offered by several suppliers, under several different trade names.

Use Patterns of MSMA and DSMA in the United States

General - MSMA and DSMA are organic arsenical herbicides derived from pentavalent arsenic. DSMA was the first herbicide in the group to be introduced commercially, but MSMA has since outpaced DSMA by a considerable margin because of its somewhat superior herbicidal effectiveness as compared to DSMA.

MSMA and DSMA (along with the other organic arsenical herbicides) are contact herbicides which are very effective against hard-to-kill grass weeds and several species of broadleaf weeds. They are relatively inexpensive, compared to many other herbicides recommended for the same weed control purposes. No other herbicides are directly comparable to the organic arsenical herbicides in regard to efficacy, low cost, and physical and chemical properties, including ease of formulation and application.

MRI and RvR Consultants (von Rümker et al. 1974) estimated MSMA and DSMA use in the United States in 1972 by region and major category. (See Table 8.)

They contend that about 23 million lb of MSMA and DSMA AI were used in the United States in 1972. Approximately 19 million lb, more than 80% of this total, are believed to have consisted of MSMA. An estimated 15.5 million pounds of MSMA and DSMA, about two-thirds of the total domestic consumption, were used in agriculture, primarily for postemergence weed control on cotton. Industrial and commercial weed control uses accounted for an estimated 4.5 million lb AI; uses by governmental agencies resulted in an additional 1.2 million lb. It is further estimated that about 1.8 million lb of MSMA and DSMA were used for residential and home garden weed control purposes. Geographically, an estimated 14.7 million lb of MSMA and DSMA AI were used in the South Central region in 1972, about 70% of the subtotal, exclusive of home garden uses for which there were no estimates available. The largest single use in the South Central region was weed control on cotton. About 3 million lb of MSMA and DSMA were used in the Southeastern states, about 1.4 million lb in the North Central, and about 1 million lb in the Southwestern states. Less than 1 million lb each were used in the Northwestern and Northeastern states. All of the figures are subtotals and do not include home, garden, and residential uses of MSMA and DSMA.

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[1] Billings, S. C., ed., Pesticide Handbook-Entoma, 25th ed., Entomological Soc. of Amer., College Park, Maryland, 312 pp. (1974).

Table 8. ESTIMATED USES OF MSMA AND DSMA IN THE UNITED STATES BY REGIONS AND CATEGORIES, 1972

	Category					
Region	Agriculture	Industrial/ commerical	Government agencies	Subtotal	Home garden	Total
	(Thousands of pounds active ingredient)					
Northeast[a]	Negl.	300	100	400		
North Central[b]	500	700	200	1,400	Geographic distribution not known	
Southeast[c]	1,800	1,000	250	3,050		
South Central[d]	12,700	1,700	250	14,650		
Northwest[e]	200	400	100	700		
Southwest[f]	300	400	300	1,000		
Total	15,500	4,500	1,200	21,200	1,800	23,000

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a/ New England States, New York, New Jersey, Pennsylvania.

b/ Ohio, Indiana, Illinois, Michigan, Wisconsin, Maine, Iowa, Missouri, North Dakota, South Dakota, Nebraska, Kansas.

c/ Maryland, Delaware, Virginia, West Virginia, North Carolina, South Carolina, Georgia, Florida.

d/ Kentucky, Tennessee, Arkansas, Louisiana, Mississippi, Alabama, Oklahoma, Texas.

e/ Montana, Idaho, Wyoming, Colorado, Utah, Washington, Oregon, Alaska.

f/ New Mexico, Nevada, Arizona, California, Hawaii.

Source: von Rümker, op. cit. (1974).

Agricultural Uses of MSMA and DSMA - Surveys on the use of pesticides by farmers in the United States were conducted by the U.S. Department of Agriculture (1964, 1966, and 1971).[1-3] Data for 1972 was obtained from the MRI and RvR Consultants study (von Rümker 1974).

Table 9 summarizes farm uses of organic arsenical herbicides from these surveys for the years 1964, 1966, 1971, and 1972. USDA data includes other arsenical herbicides.

Table 9. FARM USES OF ORGANIC ARSENICAL HERBICIDES IN THE UNITED STATES IN 1964, 1966, 1971 AND 1972

	Year			
	1972 RvR[a]	1971 USDA[b]	1966 USDA	1964 USDA
	(Thousands of Pounds AI)			
Crops	15,300	7,837	866	1,006
Other farm uses*	200	144	15	71
Total farm uses	15,500	7,981	881	1,077

* Includes fence rows, ditchbanks and other noncrop farm uses.

[a] von Rümker op. cit. (1974).

[b] U.S. Department of Agriculture Pesticide use reports for 1968, 1970, 1974.

According to USDA, the use of organic arsenical herbicides by farmers increased substantially from the mid-1960's to 1971. Table 9 shows an additional substantial increase from 1971 to 1972. USDA data, however, is not

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[1] U.S. Department of Agriculture, "Quantities of Pesticides Used by Farmers in 1964," Agricultural Economic Report No. 131, Economic Research Service (1968).

[2] U.S. Department of Agriculture, "Quantities of Pesticides Used by Farmers in 1966," Agricultural Economic Report No. 179, Economic Research Service (1970).

[3] U.S. Department of Agriculture, "Farmers' Use of Pesticides in 1971. . . Quantities," Agricultural Economic Report No. 252, Economic Research Service (1974).

directly comparable to the RvR estimates, which are based on U.S. Tariff Commission reports. USDA data is derived from interviews with farmers in selected counties throughout the United States. The interviews were conducted as part of nationwide programs to collect data on farm production expenditures. Pesticide uses data was a small segment of the overall program. The raw pesticide data obtained was expanded and adjusted to apply from the survey sample to nationwide use. The USDA reports point out that the reliability of the data is related to the quantity of pesticides used, the number of acres treated, and the importance of the crop in the region. The relative distribution of pesticides among crops and regions shown in their report is more reliable than absolute quantities for individual crops and regions. MRI believes that the actual farm use was higher than that shown by USDA survey results, so that actual farm use of MSMA and DSMA did not nearly double from 1971-1972, as Table 9 indicates.

Weed control on cotton is by far the most important agricultural use of MSMA and DSMA. Additional farm uses of the 2 compounds include weed control in bearing or nonbearing citrus groves (except in Florida). MSMA can be used in nonbearing vineyards and nonbearing deciduous fruit and nut orchards, such as apple, pear, peach, plum, prune, apricot, cherry, almond and walnut. MSMA and DSMA are also used on the farm for weed control on fallow land, on drainage ditchbanks, rights-of-way, storage areas, along fence rows, and in similar places around the farm requiring weed control.

Of the total estimated farm use of MSMA and DSMA in the U.S. in 1972, 15.5 million lb AI (Table 8), 12.7 million lb, or more than 80%, were used in the South Central states, the area in which a large share of the U.S. cotton crop is grown. An estimated 1.8 million lb of MSMA and DSMA were used on farms in the Southeastern states, and 500,000 lb or less each in the North Central, Southwestern and Northwestern states.

Industrial and Commercial Uses of MSMA and DSMA - An estimated 4.5 million lb of MSMA and DSMA AI were used in 1972 for industrial and commercial weed control purposes. In this field, MSMA and DSMA are used for postemergence control of hard-to-kill grass and broadleaf weeds, and as a silvicide in privately owned forests. Mixed with other herbicide brush killers, MSMA increases kill or dieback of woody weeds.

According to MRI and RvR estimates (von Rümker et al. 1974), about 4 million lb of MSMA were used domestically for industrial and commercial weed control purposes in 1972 and an additional 500,000 lb of DSMA were used in the same field, resulting in the total of 4.5 million lb of MSMA and DSMA shown in Table 8 for industrial and commercial weed control. By geographical region, 1.7 million lb (slightly more than one-third of the total for this category) were used in the South Central states, followed by the Southeastern states (about 1.0 million lb) and, in decreasing order of use volume, the North Central, Northwestern, Southwestern, and Northeastern states.

Government Agencies' Uses of MSMA and DSMA - MRI and RvR also studied the uses of selected pesticides, including MSMA, by governmental agencies and estimated that these agencies used about 1.0 million pounds of MSMA active ingredient in 1972. An additional 200,000 lb of DSMA were applied for weed control purposes by governmental agencies in 1972, thus accounting for the MSMA and DSMA total of 1.2 million lb AI indicated in Table 8. This volume was distributed relatively evenly throughout the entire country. The Northwestern and Northeastern states accounted for the smallest shares of the total (von Rümker et al. 1974).

Governmental agencies use MSMA or DSMA for the control of weeds along Federal, state, county or other roads; in flood control, irrigation, reclamation, or water districts; in county or city parks; on school and other premises; as a silvicide in publicly owned forests; and in many other situations where postemergent weed control is desired. Such governmental agencies often operate on tight budgets. When this is the case, MSMA and DSMA are attractive because of their relatively low cost in comparison to many other herbicides.

Home Garden Uses of MSMA and DSMA - MSMA and DSMA are the preferred herbicides for the selective control of crabgrass, nutsedge, dallisgrass, sandbur, bahiagrass, chickweed, wood sorrel and similar weeds in established lawns and turf, except St. Augustine, centipede, or carpetgrass, or dichondra lawns. Two or more repeat treatments at 14-day intervals may be necessary for satisfactory lawn weed control.

It is estimated that about 1.8 million lb of MSMA and DSMA AI were used for residential and home garden weed control in 1972. Since home and garden pesticide uses were not included in the MRI/RvR study, estimates on the geographic distribution of residential and home garden could not be made.

MSMA and DSMA Uses in California - California keeps detailed records of pesticide uses by crops and other uses which are published quarterly and summarized annually. Table 10 summarizes the uses of MSMA and DSMA in California by major crops and other uses for 1970-1973 period.

In California, organic arsenical herbicides are not subject to the special restrictions and reporting requirements imposed upon the sale and use of pesticides designated as "injurious or restricted materials." For this reason, the percentage of all MSMA and DSMA uses reported to the State Department of Agriculture and included in its statistics is probably not as high as in the case of the restricted pesticides. However, the California Department of Agriculture and others familiar with pesticide uses in the State believe that the Department's statistics do include a high percentage of the actual uses of nonrestricted pesticides.

According to these State reports (Table 10), the use of MSMA in California for all purposes increased from 181,300 lb in 1970 to 256,000 lb in 1973, with the 1971 and 1972 use volumes ranging in between. Much smaller quantities of DSMA were used, ranging from 21,800 lb in 1970 to 90,300 lb in 1971. The quantities of DSMA used in California in 1972 and 1973 were intermediate.

The combined volume of use of MSMA and DSMA in California, according to the State pesticide reports, was about 200,000 lb AI in 1970. It jumped to about 300,000 lb AI in 1971 and remained at about that level during 1972 and 1973.

The use of MSMA and DSMA on cotton in California declined from 32,400 lb in 1970 to around 12,000 lb in 1971, 1972, and 1973. The use on citrus increased steadily, from about 600 lb in 1970 to 7,700 lb in 1973. The sizable increase in the use of MSMA and DSMA on California citrus from 1972 to 1973 was probably due to the registration of the use of these herbicides in bearing citrus orchards.

MSMA and DSMA uses on "other crops" include those for which the herbicides are registered and recommended, such as nonbearing grape vineyards and deciduous fruit and nut plantings. In addition, MSMA and DSMA were used on a number of crops, including beans, celery, onions, garlic, tomatoes, rice, safflower, sorghum, sugar beets, and alfalfa, for which they are not registered or recommended Federally or within the state.

Other uses of MSMA and DSMA in California include uses in residential and industrial areas; in flood control, irrigation, and mosquito control districts; in other water resource areas; and uses by city, county, state, and Federal government agencies, and by the University of California. Some of these other uses of MSMA and DSMA in California involve applications to farmlands. Therefore, the category "other uses" in Table 10 is not comparable to the nonagricultural MSMA and DSMA use categories in Table 8.

Tables 11 through 14 present the uses of MSMA and DSMA in California in detail, by crops and other uses, number of applications, pounds of active ingredient, and number of acres treated for 1972 and 1973, the two most recent years for which such data is available. These tables expand and provide further insight into the MSMA and DSMA uses in California in 1972 and 1973 presented in summary form in the left part of Table 10.

At the present time, no other state records or publishes pesticide use data in comparable detail. Limitations of time and resources available for this task did not permit development of estimates on the uses of MSMA and DSMA by states, crops, and other uses beyond the detail provided in Table 8.

By far the largest share of MSMA and DSMA used each year was for industrial, commercial and residential weed control, and for flood and vector control. The arsenicals were also used in irrigation districts and other water resource areas and by governmental agencies. Only about 10% of the MSMA and DSMA quantities used in recent years in California was applied to cotton, citrus and other crops.

Table 10. MSMA AND DSMA USES IN CALIFORNIA BY MAJOR CROPS AND OTHER USES, 1970-1973

Crop/use	Year Product	1973		1972		1971		1970	
		MSMA	DSMA	MSMA	DSMA	MSMA	DSMA	MSMA	DSMA
		Thousand of Pounds of Active Ingredients							
Cotton		11.1	1.1	10.7	0.2	11.3	2.2	28.6	3.8
Citrus		7.7	Negl.	1.4	Negl.	1.0	Negl.	0.6	Negl.
Other crops[a/]		8.6	Negl.	4.9	2.9	4.8	0.3	11.5	0.1
Other uses[b/]		228.8	38.3	228.8	55.6	206.9	87.8	140.6	17.9
Total, all uses		256.2	39.4	245.8	58.7	224.0	90.3	181.3	21.8

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a/ Including some crops for which MSMA and DSMA are not registered or recommended, e.g., beans, celery, onions, garlic, tomatoes, rice, safflower, sorghum, sugar beets, alfalfa.

b/ Including residential and industrial areas; flood control, vector control and irrigation districts; other water resource areas; uses by city, county, state, and Federal Government agencies, and by the University of California.

Source: California Department of Agriculture, Pesticide use reports for 1970, 1971, 1972 and 1973.

Table 11. USE OF MSMA IN CALIFORNIA IN 1972, BY CROPS AND OTHER USES, APPLICATIONS, QUANTITIES, AND ACRES TREATED

Commodity	Applications	Pounds	Acres
Almond	5	913.91	437.00
Celery	11	111.80	146.60
Citrus	1	31.19	10.00
City agency		1,579.98	
Cotton	61	10,714.08	3,557.20
County agricultural commissioner		26,194.49	
County or city parks		1,124.71	
County road		20,043.89	
Federal agency		1,024.17	
Fallow (open ground)	11	2,467.51	579.00
Flood control		1,335.83	
Flowers	1	13.10	7.00
Industrial areas	4	32.41	2.75
Irrigation district		44,662.32	
Lemon	1	68.27	20.00
Lettuce (head)	1	77.20	33.00
Nonagricultural areas	180	16,002.34	3,833.76
Onion (dry)	1	202.16	14.00
Orange	52	1,332.76	944.00
Other agencies		34,853.01	
Plum	1	9.35	20.00
Pomegranate	1	124.78	40.00
Reclamation district		1,168.55	
Residential control		3,498.85	
Rice	1	20.79	10.00
Safflower	1	109.96	47.00
School district		258.06	
Sorghum	1	1.45	34.00
State highway		34,784.94	
Sugar beet	1	117.65	35.00
Turf	10	490.22	103.00
University of California		944.89	
Vector control		458.50	
Walnut	11	749.93	308.00
Water areas	29	14,452.26	200.00
Water resources		25,802.46	
Watermelon	1	1.02	24.00
Total	386	245,778.79	10,405.31

Source: California Department of Agriculture, Pesticide Use Report 1972 (1972).

Table 12. USE OF MSMA IN CALIFORNIA IN 1973, BY CROPS AND OTHER USES, APPLICATIONS, QUANTITIES, AND ACRES TREATED

Commodity	Applications	Pounds	Acres
Almond	9	2,063.08	605.00
Beans (dry edible)	1	50.61	15.00
Celery	30	883.12	684.00
Citrus	1	15.43	4.00
City agency		2,712.89	
Cotton	109	11,115.50	6,499.00
County agricultural commissioner		24,120.35	
County or city parks		3,162.40	
County road		12,518.35	
Federal agency		206.74	
Fallow (open ground)	21	2,619.54	930.25
Flood control		2,910.95	
Grape	9	1,730.27	287.00
Industrial areas	5	16.72	9.70
Irrigation district		40,119.42	
Lemon	9	579.94	544.00
Lettuce (head)	2	1.49	35.00
Nonagricultural areas	107	9,843.22	2,652.87
U - Nonagricultural areas	4	16.85	4.00
Olive	6	111.22	29.00
Orange	83	7,121.50	2,537.00
Orchard	1	31.19	10.00
Ornamentals	1	31.13	10.00
Other agencies		34,046.09	
Pomegranate	1	20.24	3.00
Reclamation district		2,568.03	
Residential control		4,510.00	
School district		855.25	
Sorghum	1	361.87	58.00
State highway		66,009.73	
Structural control		2.27	
Tomato	2	137.81	82.00
Turf	2	144.04	22.00
University of California		230.13	
Vector control		992.50	
Walnut	12	3,212.06	910.00
Water areas	23	2,805.93	207.24
U - Water areas	1	1.57	1.00
Water resources		18,367.85	
Total	440	256,247.26	16,134.06

U = Miscellaneous units.

Source: California Department of Agriculture, Pesticide Use Report 1973 (1973).

Table 13. USE OF DSMA IN CALIFORNIA IN 1972, BY CROPS AND OTHER USES, APPLICATIONS, QUANTITIES, AND ACRES TREATED

Commodity	Applications	Pounds	Acres
Almond	4	402.20	435.00
City agency		2,048.51	
Cotton	4	160.98	230.00
County agricultural commissioner		14,310.25	
County or city parks		618.49	
County road		867.78	
Federal agency		1,109.61	
Flood control		8,564.99	
Garlic	2	661.50	75.00
Industrial areas	2	4.82	1.50
Irrigation district		3,153.44	
Nonagricultural areas	23	1,172.56	582.59
Onion (dry)	8	1,794.24	299.00
Orange	1	7.39	20.00
Other agencies		1,928.14	
Pasture/rangeland	1	0.02	4.00
Recreational areas	1	1.84	1.00
Residential control		2,508.90	
School district		3,081.87	
State highway		14,064.75	
Structural control		39.44	
University of California		505.62	
Water areas	4	35.83	32.00
Water resources	—	1,624.10	
Total	50	58,667.27	1,680.09

Source: California Department of Agriculture, Pesticide Use Report 1972 (1972).

Table 14. USE OF DSMA IN CALIFORNIA IN 1973, BY CROPS AND OTHER USES, APPLICATIONS, QUANTITIES, AND ACRES TREATED

Commodity	Applications	Pounds	Acres
City agency		1,238.34	
Cotton	11	1,124.76	867.00
County agricultural commissioner		9,477.26	
County or city parks		1,991.51	
County road		850.64	
Federal agency		830.31	
Fallow (open ground)	4	120.60	45.25
Flood control		2,107.16	
Grape	1	0.04	86.00
Industrial areas	5	25.20	8.62
Irrigation district		627.15	
Nonagricultural areas	12	230.55	31.60
Other agencies		910.28	
Residential control		1,518.02	
School district		2,151.91	
State highway		14,965.26	
University of California		355.03	
Water resources		923.31	
Total	33	39,447.33	1,038.47

Source: California Department of Agriculture, Pesticide Use Report 1973 (1973).

References

The Ansul Company, Weeds Controlled by MSMA, Marinette, Wisconsin (1972).

Billings, S. C., ed., Pesticide Handbook-Entoma, 25th ed., Entomological Soc. of Amer., College Park, Maryland, 312 pp. (1974).

California Department of Agriculture, Pesticide use reports for 1970, 1971, 1972 and 1973.

U.S. Bureau of the Census, U.S. Exports, Schedule B, Commodity by Country, Section 599, 2080 Report FT410 (1972).

U.S. Department of Agriculture, Farmers' Use of Pesticides in 1971...Quantities, Agricultural Economic Report No. 252, Economic Research Service (1974).

U.S. Department of Agriculture, Quantities of Pesticides Used by Farmers in 1964, Agricultural Economic Report No. 131, Economic Research Service (1968).

U.S. Department of Agriculture, Quantities of Pesticides Used by Farmers in 1966, Agricultural Economic Report No. 179, Economic Research Service (1970).

U.S. Environmental Protection Agency, EPA Compendium of Registered Pesticides, Vol. I, p. m - 9.

U.S. Tariff Commission, Synthetic Organic Chemicals, U.S. Production and Sales, T.C. Publication 681 (1971, 1972, 1973).

von Rümker, R. E. W. Lawless, and A. F. Meiners, Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides, Final Report for Council on Environmental Quality, Washington, D.C., Contract No. EQC-311 439 pp. (1974).

PART III. EFFICACY AND PERFORMANCE REVIEW

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This section contains a general assessment of the efficacy of MSMA and DSMA. Studies on the production of MSMA and DSMA in the United States, as well as an analysis of their use patterns at the regional level and by major crop, were conducted as part of the Scientific Review (Part II) of this report. The section summarizes rather than interprets data reviewed.

Introduction

Efficacy tests are intended to determine a product's ability to actually control a specified target pest or produce a specified plant action. Data on actual usefulness is also evaluated since the effectiveness and usefulness of a given herbicide can differ. A herbicide can be effective in controlling a target weed species, but some adverse effect such as the death of desirable plants would negate its usefulness.

The following criteria were used to review efficacy tests: types of crops involved, target pests and population level, quantitative and qualitative changes in yields, and rates and time application, in accordance with conditions on the product's label. Data on higher dosages than recommended was also reviewed to allow an estimate of safety between effective pesticide levels and those which injure the crop. Some of these factors are crop variety, geographical location of the test, year of the test, methods of application, numbers of sampling replicates, climatic conditions prior to treatment, at treatment, and right after treatment, edaphic (soil) factors, and many others. Statistical validity of tests was also considered.

This review presents a range of the potential benefits to be derived from the use of MSMA and DSMA for weed control of specific pests in a specific crop area.

The use of the methanearsonates for weed control in both crop and noncrop areas has been recognized and accepted throughout the agricultural industry. Although a considerable number of methanearsonates exist, DSMA and MSMA are the two most commonly known and widely used.

DSMA and MSMA are primarily known for control of Johnson grass in cotton and noncrop areas. Undoubtedly, Johnson grass is the most economically important weed controlled by these arsenicals. Yellow nutsedge and purple nutsedge are the second most important weeds treated with these products. Other important weeds controlled include dallisgrass, sandbur, and field sandbur.

In addition to control of many weedy grasses, broad-leaved weeds, such as cocklebur, pigweed, ragweed, puncturevine, ivy-leaved morning glory, and annual morning glory may be controlled using DSMA or MSMA. Best control is obtained on these weeds if the application is made while the weeds are in an early stage of growth.

Other familiar weeds susceptible to these herbicides include green foxtail, yellow foxtail, giant foxtail, witchgrass, crotalaria or rattlebox, barnyard or watergrass, and tules or bulrush.

The efficacy of MSMA and DSMA depends on the timing, number of applications, temperature and type of surfactant used. Widiger (1966)[1/] reported that repeat applications are needed for control of the deep-rooted perennials and that mature or nearly mature weeds in noncrop areas require increased spray volumes to obtain adequate coverage. He also found that temperatures below 60°F appear to decrease the effectiveness of DSMA and MSMA and that sunlight appears to be as important to the action of these herbicides as temperature. The use of a surfactant is recommended also since it increases the effectiveness of these herbicides.

Efficacy in Noncrop Uses

Johnson Grass Control - Johnson grass is a serious weed problem, particularly in the southern states. Both MSMA and DSMA have been found to effectively control Johnson grass, when used as postemergent herbicides. Their attractiveness is due to their ability to attack and decay the rhizomes of the grass, preventing regrowth. The rate and number of applications are important to control.

Most tests indicated that single applications of methanearsonates provide only short-term control. Williams and Horsnail (1972)[2/] evaluated MSMA along railroads, roadsides, ditchbanks and on waste ground at various locations in the South. These tests were conducted with single applications of 10 lb/acre MSMA. The results of three roadside test sites showed 95 to 97% control 31 to 33 days after application, dropping to 17 to 80% control in 89 to 139 days after application. Along a ditchbank in Louisiana, control dropped from 81% in 41 days after application to 4% in 70 days after application. Similar results were obtained along railroads and waste ground.

Millhollon (1970)[3/] reported that an initial application of MSMA in the spring killed the foliage, but many stools survived and produced abundant new foliage from rhizomes in approximately 4 weeks. A second application of MSMA at either 2.5 or 4 lb/acre destroyed this regrowth and apparently killed

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[1/] Widiger, R. E., "Weeds Controlled by the Methanearsonates," Proc. South. Weed Sci. Soc., 19:51-56 (1966).

[2/] Williams, D. J., and G. B. Horsnail, "Asulam for Johnson Grass Control in Noncrop Situations," Proc. South. Weed Sci. Soc., 25:347-353 (1972).

[3/] Millhollon, R. W., "MSMA for Johnson Grass Control in Sugarcane," Weed Sci., 18:333-336 (1970).

most stools of Johnson grass since the authors observed very little new growth thereafter. Roeth (1972)[1] also found that 2 applications of MSMA at 3 lb/acre reduced rhizome yield by 76%.

Sckerl et al. (1966)[2] evaluated the efficacy of these arsenicals at various rates and number of applications in the greenhouse and in tests along highway rights-of-way in Arkansas. The authors reported that poor control was evidenced when DSMA was applied at a rate of 1 lb/acre and that rates ranging from 2 to 5 lb/acre gave 78 to 80% control with no significant difference among these rates. Regardless of the rate, some regrowth occurred. Another test showed that 3 applications of DSMA gave 91 to 93% seasonal control at rates of 3 and 4 lb/acre, whereas MSMA gave 83 to 90% seasonal control with 3 applications of 2, 3, and 4 lb/acre. One application of MSMA or DSMA the following season controlled 90% of the Johnson grass regrowth.

Bermuda grass is not affected by the arsenicals and often becomes the dominant grass upon control of Johnson grass. Millhollon (1969)[3] evaluated MSMA for control of Johnson grass on drainage ditchbanks in Louisiana sugarcane in 1965 and 1966. He found that 3 applications of MSMA in 1965 at rates varying from 3.6 to 7.2 lb/acre substantially reduced the stand of Johnson grass. Infestation in the following spring varied from 3 to 9%. Two treatments in 1966 resulted in a reduction to 1 to 2% in the following spring. Bermuda grass became dominant on the treated plots resulting in a 50% infestation the following year.

Nutsedge Control - Purple and yellow nutsedge are important perennial weed species in temperate and tropical areas and are common in many field crops, orchards and vegetables. They often benefit from the lack of competition when other weeds are controlled by herbicides.

Leyden (1967)[4] evaluated MSMA for control of nutsedge in citrus orchards in Texas and found that MSMA in 4 applications at 30-day intervals resulted in complete topkill a few days after application. However, 60% regrowth was experienced 30 days after the fourth application.

1/ Roeth, F. W., "Herbicidal Control of Johnson Grass in Noncropland," Proc. North Cent. Weed Control Conf., 27:56-57 (1972).

2/ Sckerl, M. M., R. E. Frans, and A. E. Spooner, "Selective Inhibition of Johnson Grass with Organic Arsenicals," Proc. South. Weed Sci. Soc., 19:351-357 (1966).

3/ Millhollon R. W., "Control of Johnson Grass on Drainage Ditchbanks in Sugarcane," Weed Sci., 17:370-373 (1969).

4/ Leyden, R. F., "Control of Nutsedge in Texas Citrus Orchards," Proc. South. Weed Sci. Soc., 20:130-133 (1967).

Keeley and Thullen (1971)[1] found that an application of 3 lb/acre of MSMA provided significantly better control of purple nutsedge than DSMA. Regrowth was 89% in 3 weeks after application of DSMA and 11% in 3 weeks after application of MSMA. Three applications of these herbicides resulted in a 57% regrowth 1 week after the last application of DSMA and a 9% regrowth with MSMA. In another test it was found that purple nutsedge was more difficult to control than the yellow.

Jagshitz (1975) [2] found that 2 postemergent treatments of DSMA at 4 lb AI/acre applied in early summer, 1974, provided excellent control (96%) of yellow nutsedge in Kentucky bluegrass, but only good control (84%) in a soil area. Three applications at 4 lb AI/acre gave excellent control in both areas, 96% and 93%, respectively. Turfgrass injury was slight. Two or 3 applications of DSMA in midsummer, 1974, also gave excellent control in Kentucky bluegrass, 99% and 98%, respectively, but turfgrass injury was considered objectionable.

Efficacy in Crop Uses

Weed Control on Cotton - MSMA and DSMA are registered for directed application on cotton for postemergent control of a variety of broad-leaved weeds, grasses and morning glory. Most topical applications are not Federally registered, but some states are reported to have registered this method of application. DSMA has been the most common arsenical, but the recent trend is toward MSMA use. One commercial formulation of DSMA is Federally approved and registered for topical application with either ground or aerial equipment.

Hamilton and Arle (1970)[3] evaluated directed applications of DSMA and MSMA on irrigated cotton at University of Arizona experimental stations and found that broadleaf weed control averaged 100% when 3 to 4 direct applications of DSMA or MSMA were made. Grass control averaged 92% with DSMA and 91% with MSMA. These tests were averaged for a 3-yr period and included weeds and grasses such as browntop panicum, junglerice, barnyard grass, red spangletop, Wright ground cherry, palmer amaranth and wooly morning glory. Some localized foliage chlorosis or burning was evidenced after the first application.

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[1] Keeley, P. E., and R. J. Thullen, "Control of Nutsedge with Organic Arsenical Herbicides," Weed Sci., 19:601-606 (1971).

[2] Jagshitz, J. A., "Postemergent Crabgrass and Nutsedge Control in Turfgrass with Herbicides," Proc. Northeast Weed Sci. Soc., 29:376-381 (1975).

[3] Hamilton, K. C., and H. F. Arle, "Directed Applications of Herbicides in Irrigated Cotton," Weed Sci., 18:85-88 (1970).

Arle and Hamilton (1971)[1] evaluated the effects of single or repeated topical applications of MSMA and DSMA at rates of 2.2 (the recommended rate), 4.5, 6.7, and 9.0 kg AI/ha on irrigated cotton over a 4-yr period. In 1966, 1967, 1968, and 1969, single topical applications of MSMA and DSMA at the given rates were applied to cotton plants 2, 4, 6 and 8 weeks after emergence when plants measured 5, 10, 20, and 30 cm high, respectively. In 1968 and 1969, MSMA and DSMA, at rates of 2.2 and 6.7 kg AI/ha, were applied as topical sprays 1, 2, 3, or 4 times at 2-week intervals. In 1967 only DSMA was applied. Untreated cotton height averaged 20, 30, 46 and 71 cm tall at the 4 times of application, respectively. There were no significant differences in yield among rates and dates with single applications of DSMA. Single applications of MSMA reduced cotton yields, but only when applied at later dates or higher rates than is recommended. MSMA applied at recommended rates and times of application did not significantly reduce cotton yield. All single topical applications of MSMA and DSMA reddened cotton stems and petioles; these symptoms were more noticeable with MSMA than DSMA. In most cases these symptoms were only temporary and did not affect plant maturity and cotton yield, except under the conditions previously mentioned. Repeated topical applications of MSMA and DSMA discolored or burned cotton foilage, reddened the stems, and stunted the plants in varying degrees in relation to the rate and number of applications. Two or more topical applications of MSMA at the recommended rate of 2.2 kg AI/ha significantly reduced cotton yields as compared to one application of MSMA. Repeated topical applications of MSMA or DSMA at this rate did not affect length, strength,or fineness of fiber, boll weight or seed per boll, but did decrease lint percentage. Different varieties of cotton were used each year, but DSMA, at the recommended rate, did not significantly reduce cotton yield within any given year without 3 or more applications. Single or repeated applications of MSMA affected cotton growth more than did DSMA. Commercial formulations of MSMA and DSMA (specific formulation not given) were mixed in 374 l/ha of water to which 0.5% of blended surfactant was added (alkarylpolyoxyethylene glycoles, free fatty acids, and isopropanol).

Hogue (1971)[2] compared directed topical applications for MSMA on cotton in Mississippi and found that there were no significant differences in weed control between the 2 application methods of the same treatments when based on hoe labor requirements. Weed control of sida, pigweed, purslane, prostrate spurge, spotted spurge, and morning glory was studied. An initial topical application of MSMA at 2 lb AI/acre applied to cotton plants 3 to 6 in tall and then reapplied 2 weeks later did not significantly reduce cotton height compared to directed applications of MSMA at the same rates and times of application. However topical applications of MSMA significantly decreased cotton yields as compared to directed applications of the same treatment. The compounds were mixed in water and applied at a rate of 20 gal/acre. The mixture contained 0.25% nonionic surfactant plus an unspecified formulation of MSMA.

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[1] Arle, H. F., and K. C. Hamilton, "Topical Applications of DSMA and MSMA in Irrigating Cotton," Weed Sci., 19:545-547 (1971).

[2] Hogue, C. W., "Directed Versus Topical Application of Herbicide Combinations in Cotton," Proc. South. Weed Sci. Soc., 24:93-98 (1971).

Hogue (1973)[1] conducted experiments from 1968 to 1971 to evaluate postemergent weed control with selected herbicides. He reported that 1 direct application of MSMA per year on 3- to 6-in cotton resulted in an average reduction of 29 hr of hoe labor per acre in the 1970 to 1971 season. A single application of 2.0 lb AI/acre MSMA resulted in 54% control of broad-leaved weeds, grasses and morning glory for the 1969 to 1971 period when applied to 6- to 9-in cotton. Under the same conditions DSMA resulted in a 51% control. Average yields increased with 2 applications of MSMA but were not significantly different with a single application of MSMA or DSMA.

Baker et al. (1969)[2] studied the effects of timing and method of application of MSMA and DSMA on cotton in field experiments in California, Arizona, and Mississippi. Rates of application were either 2 or 3 lb AI/acre of the salts and either 2 or 3 applications were made to treated plots. Cotton was highly tolerant of directed spray treatments of MSMA and DSMA, and yields were not reduced. A topical application to cotton 2 to 4 in tall slightly reduced yields, but single topical applications made at later stages of growth to other plants caused progressively severe reductions in yields and delayed maturity, especially when cotton plants were in the early square and early bloom stage.

Havelka and Merkle (1967)[3] found that lint yields were not affected by a topical application of DSMA (3 lb AI/acre) or MSMA (2 lb AI/acre) when sprayed at the early square stage, but were severely reduced by treatment at blooming, which is a later application time than recommended.

Jeffery et al. (1972)[4] also found that cotton yields were not reduced by a topical application of MSMA or DSMA except when applied at the bloom stage. A rate of 2 lb AI/acre was used for both chemicals.

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[1] Hogue, C. W., "Postemergence Weed Control in Cotton with Linuron and Dinoseb," Proc. South. Weed Sci. Soc., 26:135-141 (1973).

[2] Baker, R. S., H. F. Arle, H. J. Miller, and J. T. Holstun, "Effects of Organic Arsenical Herbicides on Cotton Response and Chemical Residues", Weed Sci. 17(1):37-40 (1969).

[3] Havelka, U. D., and M. G. Merkle, "Arsenic Residues in Cotton and Johnsongrass," Proc. South. Weed Sci. Soc., 22:51-57 (1969).

[4] Jeffery, L. S., T. McCutchen, and P. E. Hoskinson, "Effects of DSMA and MSMA on Cotton," Tenn. Farm and Home Sci., Progress Report No. 84, pp. 19-21 (1972).

Weed Control on Wheat - Wild oats are a common weed pest in barley and wheat. Widiger and Klosterboer (1967)[1] conducted several tests to determine the phytotoxicity of MSMA to wheat and wild oats and to evaluate rates of application and their effect on yields. The results showed that one application of MSMA gave good control of wild oats, yellow foxtail, green foxtail and wild mustard. Wild buckwheat showed early chlorosis and stunting but recovered and was not controlled. The results of 2 tests showed that MSMA increased wheat yields by 8.0 and 8.6 bu/acre over the untreated check yield of 24.6 bu/acre.

Weed Control on Soybeans - Cocklebur, pigweed and Johnson grass are major weed pests in soybeans, often lowering quality and yield. MSMA effectively controls Johnson grass but is highly toxic to soybeans.

McWhorter (1970)[2] evaluated a recirculating spray system for control of Johnson grass in soybeans. The results showed between 70 and 75% control at harvest when 3 to 4 lb of MSMA were applied per acre. Some injury to the beans was evidenced; however, yields increased when compared to a cultivated control by 2.0 to 8.0 bu/acre.

Connell and Derting (1973)[3] also evaluated MSMA for control of various weeds in soybeans. Results of tests at Schlater, Mississippi, using MSMA at 6.0 lb/acre, showed good control of seedling Johnson grass.

Weed Control on Citrus Crops - Herbicide-treated citrus orchards promote faster tree growth; offer less mechanical injury to fruit, branches and roots; and require less fertilizer and water than cultivated orchards. Klosterboer (1974)[4] evaluated several herbicides in grapefruit orchards for phytotoxicity, defoliation, fruit abscission and yield. The results showed defoliation (6.7%) and fruit abscission (9.2%) which were slightly less than the weeded control.

MSMA and DSMA are not Federally registered or accepted. However, the herbicides are registered for state usage.

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[1] Widiger, R. E., and A. D. Klosterboer, "The Use of MSMA to Control Certain Problem Weeds in Wheat and Barley," Proc. North Cent. Weed Cont. Conf., 22:57 (1967).

[2] McWhorter, C. G., "A Recirculating Spray System for Postemergence Weed Control in Row Crops," Weed Sci., 18:285-287 (1970).

[3] Connell, J. T., and C. W. Derting, "Glyphosate Performance on Johnson Grass and Associated Weed Species in No Tillage Soybeans," Proc. South. Weed Sci. Soc., 26:51-56 (1973).

[4] Klosterboer, A. D., "Phytotoxicity of Glyphosate, MSMA and Paraquat to Bearing Citrus," Proc. South. Weed Sci. Soc., 27:166-169 (1974).

Weed Control on Sugarcane - Johnson grass is the most troublesome weed in Louisiana sugarcane. Often a planting must be abandoned at the end of the first ratoon crop because of the heavy infestation of Johnson grass.

Millhollon (1970) conducted experiments between 1966 and 1968 to evaluate the use of MSMA for control of Johnson grass in sugarcane. The results showed that 2 applications of 4 lb/acre MSMA resulted in 96% control of Johnson grass over 3 years whereas only one application resulted in 59% control. Yields of sugar increased an average of 85% over the untreated check plot.

The initial application of MSMA was only slightly phytotoxic to sugarcane with temporary mild leaf chlorosis and stunting as the usual symptoms. The second application was more phytotoxic as relatively large areas of many leaves were necrotic after treatment and sugarcane was moderately stunted for several weeks.

References

Arle, H. F., and K. C. Hamilton, "Topical Applications of DSMA and MSMA in Irrigating Cotton," *Weed Sci.*, 19:545-547 (1971).

Baker, R. S., H. F. Arle, J. H. Miller, and J. T. Holstun, Jr., "Effects of Organic Arsenical Herbicides on Cotton Response and Chemical Residues," *Weed Sci.*, 17:37-40 (1969).

Connell, J. T., and C. W. Derting "Glyphosate Performance on Johnson Grass and Associated Weed Species in No Tillage Soybeans," *Proc. South. Weed Sci. Soc.*, 26:51-56 (1973).

Hamilton, K. C., and H. F. Arle, "Directed Applications of Herbicides in Irrigated Cotton," *Weed Sci.*, 18:85-88 (1970).

Havelka, U. D., and M. G. Merkle, "Arsenic Residues in Cotton and Johnson-grass," *Proc. South. Weed Sci. Soc.*, 22:51-57 (1969).

Hogue, C. W., "Directed Versus Topical Application of Herbicide Combinations in Cotton," *Proc. South. Weed Sci. Soc.*, 24:93-98 (1971).

Hogue, C. W., "Postemergence Weed Control in Cotton with Linuron and Dinoseb," *Proc. South. Weed Sci. Soc.*, 26:135-141 (1973).

Jagshitz, J. A., "Postemergent Crabgrass and Nutsedge Control in Turfgrass with Herbicides," *Proc. South. Weed Sci. Soc.*, 29:376-381 (1975).

Jeffery, L. S., T. McCutchen, and P. E. Hoskinson, "Effects of DSMA and MSMA on Cotton", *Tenn. Farm and Home Sci.*, Prog. Rept. No. 84, pp. 19-21 (1972).

Keeley, P. E., and R. J. Thullen, "Control of Nutsedge with Organic Arsenical Herbicides," *Weed Sci.*, 19:601-606 (1971).

Kinsella, N. J., "Environmental Impact and Public Response to an Intensive Spraying Program," *Proc. South. Weed Sci. Soc.*, 26:334-338 (1973).

Klosterboer, A. D., "Phytotoxicity of Glyphosate, MSMA, and Paraquat to Bearing Citrus," *Proc. South. Weed Sci. Soc.*, 27:166-169 (1974).

Leyden, R. F. "Control of Nutsedge in Texas Citrus Orchards," *Proc. South. Weed Sci. Soc.*, 20:130-133 (1967).

McWhorter, C. G., "A Recirculating Spray System for Postemergence Weed Control in Row Crops," *Weed Sci.*, 18:285-287 (1970).

Millhollon, R. W., "Control of Johnson Grass on Drainage Ditchbanks in Sugarcane," *Weed Sci.*, 17:370-373 (1969).

Millhollon, R. W., "MSMA for Johnson Grass Control in Sugarcane," Weed Sci., 18:333-336 (1970).

Offutt, J. R., "Chemical Weed Control Replaces Mechanical Weed Control in Ditch Maintenance," Proc. Calif. Weed Conf., 19:32-37 (1967).

Roeth, F. W., "Herbicidal Control of Johnson Grass in Noncropland," Proc. North Cent. Weed Control Conf., 28:56-57 (1972).

Sckerl, M. M., R. E. Frans, and A. E. Spooner, "Selective Inhibition of Johnson Grass with Organic Arsenicals," Proc. South Weed Sci. Soc., 19:351-357 (1966).

Widiger, R. E., "Weeds Controlled by the Methanearsonates," Proc. South. Weed Sci. Soc., 19:51-56 (1966).

Widiger, R. E., and A. D. Klosterboer, "The Use of MSMA to Control Certain Problem Weeds in Wheat and Barley," Proc. North Cent. Weed Control Conf., 22:55-57 (1967).

Williams, D. J., and G. B. Horsnail, "Asulam for Johnson Grass Control in Noncrop Situations," Proc. South. Weed Sci. Soc., 25:347-353 (1972).